

**METAL FLUXES
IN
SPRUCE AND BEECH
FOREST ECOSYSTEMS
OF SOUTH SWEDEN**

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**Department of Ecology
Plant Ecology
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To Yvonne, Björn and Jesper

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		Abstract Deposition and element dynamics in forest ecosystems were studied from 1978 to 1984 in four different forest lokalities in the southernmost part of Sweden and on the Swedish west coast. Lysimeter technique was used for the study of soil element dynamics (Na, K, Mg, Ca, Fe, Mn, Al, Cu, Zn, Cd, Pb, Cr, Ni, H, pH and dissolved organic C). The ecosystems studied were beech, spruce and regeneration areas (from spruce) on podzol and brown forest soil. Metal budgets of two mature spruce forest ecosystems on well developed podzols were calculated. The influence of tree species and management on element dynamics in a brown forest soil and a podzol as well as influence of experimental acidification on a podzol were considered. The leaching of some metals (Fe, Cu, Pb, Cr and Al-org.) seem to be associated with the leaching of organic matter. These complexes are leached from the A horizon in considerable amounts. They are precipitated in the B horizon and only small amounts are transported further downward. By contrast, the leaching of Na, Mg, Ca, Mn, Cd, Zn, Ni and Al-inorg. increases with increasing soil depth. The highest concentrations in the soil solution are often found at the transition to the C horizon or even deeper in the soil. The loss of base cations is greater from a brown forest soil than from a more acid podzol. The reverse is true of Al. Different buffer systems are reacting against increases in soil acidity in these two soil types. The soil solution acidity and concentrations of metals are usually higher in the spruce stand than in an adjacent beech stand, as are the net losses of many metals. In an adjacent open regeneration area the soil is much less acid and the leaching of metals much lower.	
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The dissertation is based on the following three papers:

- I. Bergkvist, B.: 1986, Soil solution chemistry and metal budgets of spruce forest ecosystems in s. Sweden. *Water, Air and Soil Pollution* (submitted).
- II. Bergkvist, B.: 1986, Leaching of metals from a spruce forest soil as influenced by experimental acidification. *Water, Air and Soil Pollution* (in press).
- III. Bergkvist, B.: 1986, Leaching of metals from forest soils as influenced by tree species and management. *Forest Ecology and Management* (submitted).

The papers are referred to by the above Roman numerals.

Introduction

Deposition and element dynamics in forest ecosystems were studied from 1978 to 1984 in four different forest localities in the southernmost part of Sweden and on the Swedish west coast. Lysimeter technique was used for the study of soil element dynamics. The ecosystems studied were beech, spruce and regeneration areas (from spruce) on podzol and brown forest soil. Metal budgets of two mature spruce forest ecosystems on well developed podzols were calculated (I). The influence of tree species and management on element dynamics in a brown forest soil and a podzol (III) as well as the influence of experimental acidification on a podzol were considered (II).

Objectives:

This study is part of a larger project, on deposition and cycling of metals in nature, co-ordinated by G. Tyler (Dept. of Ecology, Lund) and financed by the Swedish Environmental Protection Board.

The objectives of the study are as follows:

A) On mature spruce forest ecosystems:

a) to quantify the deposition and biomass cycling of metals (sodium, potassium, magnesium, calcium, iron, manganese, aluminium, copper, zinc, cadmium, lead, chromium and nickel) and hydrogen ions;

b) to quantify the ecosystem budgets of metals;

c) to quantify the metal budgets of different soil horizons;

d) to study the differences in concentrations of metals, hydrogen and soluble organic compounds in soil solution from the various soil horizons;

e) to study the release and re-precipitation of organic compounds in the soil.

f) by experimental acidification to evaluate to what extent an accelerated but moderate acidification of a podzolized forest soil can cause high concentrations of metals in soil solutions and to quantify metal losses from the soil.

B) In the study of a brown forest soil and a podzol, each with adjoining stands of Norway spruce (*Picea abies*), European beech (*Fagus sylvatica*) and open regeneration areas from spruce, to quantify the influence of tree species and land management on soil acidification processes and on the leachability and annual flux of metals in the different soil types.

Results

Paper I. The fluxes of metals (Na, K, Ca, Mg, Fe, Mn, Al, Cu, Zn, Pb, Cd, Cr and Ni) in two spruce forest soils in SW. Sweden (Värsjö, c. 30 km NW Hässleholm and Gårdsjön, c. 50 km N Göteborg) were quantified using lysimeter technique. Fluxes in precipitation (dry and wet), throughfall, litterfall and annual accumulation in biomass were also quantified, as well as stores in soil and biomass. The metal concentrations of the soil solutions varied greatly according to season. The leaching of some metals (Fe, Cu, Pb, Cr and organic forms of Al) was associated with the leaching of organic matter. These complexes were leached from the A horizon in considerable amounts. They precipitated in the upper B horizon and only small amounts were transported further downward. By contrast, the leaching of Na, Mg, Ca, Mn, Cd, Zn, Ni and inorganic forms of Al increased with increasing soil depth. The concentrations of these metals also increased with the soil solution acidity. The highest concentrations were often found at the transition to the C horizon. The amounts of Na, K, Mg, Ca, Mn, Al, Zn, Cd, Cr and Ni leached from the rooting zone were found to be larger than the amounts deposited from the atmosphere, the main source of these metals being the mineral soil. The reverse was true of Pb, Cu and Fe, the sink being the upper part of the B horizon.

Paper II. In the southern study area (Värsjö) of paper I, acidified ($\text{H}_2\text{SO}_4 + \text{HNO}_3$, 3:1) throughfall waters (pH 3.16 and 3.40 as volume weighted means) or control (untreated throughfall water, mean pH 3.72) were applied for 3.5 yr by an automatic irrigation device to lysimeters containing podzolized spruce forest soils of 0-5, 0-15 and 0-35 cm soil depth. The total volume of the leachates was

measured, together with their pH and total content of DOC, Na, K, Ca, Mg, Fe, Mn, Al, Cu, Zn, Cd and Pb and the initial amounts of metals and H in the soil. Most of the H^+ added with the throughfall waters was retained within the soil. Concentrations and fluxes of Mg, Ca, Mn, Zn and Cd in the soil were significantly increased by addition of acidified throughfall waters; K was less affected. As a consequence of lowered flux of DOC in the A horizon as acid input increased, Fe, Al, Cu, and Pb fluxes also decreased. The mobility of these metals in the A horizon was shown to be regulated mainly by the formation of water-soluble organic compounds rather than directly by pH variations. Compared to the control, the additional annual loss of Mg from the soil profile in the most acid treatment was c. 10% of the currently exchangeable amount.

Paper III. The leaching of metals (Na, K, Mg, Ca, Fe, Mn, Al, Cu, Zn, Cd, Pb, Cr and Ni) in a brown forest soil (Sjöbo) and a podzol (Horröd) with adjacent stands of spruce, beech and an open regeneration area were quantified using lysimeter technique. The two localities differed in soil properties: a glaci-fluvial sand deposit at Sjöbo; acid glacial till, poor in carbonates, at Horröd. Generally, the leaching of base cations was greatest from the brown forest soil, while the leaching of Al was greater from the podzol. Soil solution pH was lowest in the spruce forests, highest in the regeneration areas. The spruce increased the soil acidification and leaching rates of metals most pronouncedly in the podzol. Soil acidification and leaching of metals were usually less under beech than under spruce. Metal concentrations in the soil solution were generally lowest in the regeneration areas, as was the outflow of metals. In an opening outside the spruce canopy at Horröd soil acidification did not penetrate as deep as beneath the canopy; also the metal flux was considerably lower in the opening. Aluminium was the metal most clearly affected by variations in soil acidity in the spruce soil at Sjöbo and in all soils at Horröd. The solubility of Al increased suddenly within a small pH range (4.5-4.0) in the B horizon. The concentration of Al in soil solution increased from 2 to 10 mg l⁻¹ when pH decreased from 4.4 to 4.2. In the brown forest soil at Sjöbo, particularly in the beech stand and in the regeneration area, the increase of base cation concentrations corresponded to the soil acidity in this pH range.

Conclusions

Emerging from conditions prevailing in south Sweden, the conclusions are as follows:

A. In mature spruce forest ecosystems:

1. Lead, copper, iron and aluminium are transported from the A horizon to the B horizon by soluble organic matter. Conditions favouring dissolution of organic compounds also favour this transport.

2. The release of sodium, magnesium, calcium, zinc and cadmium from the A horizon will increase with the soil acidity. These elements are released throughout the soil profile and, usually, soil solution concentrations continue to increase at least through the B horizon.

3. The precipitation of iron and lead with organic matter in the upper B horizon is almost complete. Organic forms of aluminium are also precipitated in the B horizon.

4. An inorganic aluminium species will be released from the mineral soil and increases in concentration through the B horizon.

5. The two forests are accumulating iron, copper and lead. In the Värnsjö forest chromium is almost at balance, as is manganese at Gårdsjön.

6. The two forests are losing significant quantities of sodium, potassium, magnesium, calcium, aluminium, zinc, cadmium and nickel to the drainage water. The Värnsjö forest is also losing manganese and the Gårdsjön forest chromium.

7. Experimental acidification may increase the concentrations of several metals in the soil solution, e.g., calcium, magnesium, manganese, zinc, cadmium and (as has been shown elsewhere) eventually also aluminium. Because of increased losses of nutrients, and because there are indications that the soil weathering rate does not keep pace with these losses, there is a risk that exchangeable stores are decreasing due to acid deposition, which may lead to nutrient deficiency for plants. The concentrations of e.g. cadmium and aluminium are increased to such an extent that risks of root injury cannot be disregarded.

B. Both the soil and the vegetation type seem to be of great importance to the soil acidification and the metal leaching rates:

1. The loss of base cations (and the leaching rate of several other metals) is greater from a brown forest soil (being mainly in the base-cation exchange buffer range) than from a podzol (being in the aluminium buffer range). The reverse is true of aluminium.

2. The soil in open regeneration areas is much less acid and the leaching rates of metals are much lower than in the adjacent spruce or beech stands with same parent mineral soil.

3. In spruce stands the soil acidity is greater and penetrates deeper than in adjacent beech stands with the same parent mineral soil.

4. Brown forest soil with spruce and beech differs chemically. In a spruce stand the release of aluminium is the main buffer of soil acidity. Cation release is the main buffer reaction in a beech stand with the same parent mineral soil.

5. The soil solution concentrations of metals are usually, though not always, higher in spruce stands than in adjacent beech stands, as is the net loss of many metals.

6. Below a spruce canopy, the deeper soil horizons are distinctly more acid and the leaching rates of metals considerably greater than in an opening outside the canopy in the forest.

C. It is reasonable to claim that the use of less acidifying tree species than spruce, in areas exposed to air pollutants, would reduce nutrient losses from soils, lower the soil solution concentrations of toxic elements and counteract soil acidification. However, if the acid deposition were reduced, the acidifying influence of spruce would also diminish.

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SOIL SOLUTION CHEMISTRY AND METAL BUDGETS OF SPRUCE FOREST ECOSYSTEMS IN S. SWEDEN.

BO BERGKVIST

Department of Ecology (Plant Ecology), University of Lund , Östra Vallgatan 14, S-223 61 Lund, Sweden.

Abstract. The fluxes of metals (Na, K, Ca, Mg, Fe, Mn, Al, Cu, Zn, Pb, Cd, Cr and Ni) in two spruce forest soils in S. Sweden were quantified using lysimeter technique. Amounts in precipitation (dry and wet), throughfall, litterfall and annual accumulation in biomass were also quantified, as well as stores in soil and biomass. The metal concentrations of the soil solutions varied greatly according to season. The leaching of some metals (Fe, Cu, Pb, Cr and organic forms of Al) was associated with the leaching of organic matter. These complexes were leached from the A horizon in considerable amounts. They were precipitated in the upper B horizon and only small amounts were transported further downward. By contrast, the leaching of Na, Mg, Ca, Mn, Cd, Zn, Ni and inorganic forms of Al increased with increasing soil depth. The concentrations of these metals also increased with increasing soil solution acidity. The highest concentrations were often found at the transition to the C horizon. The amounts of Na, K, Mg, Ca, Mn, Al, Zn, Cd, Cr and Ni leached from the rooting zone were found to be larger than the amounts deposited from the atmosphere, the main source of these metals being the mineral soil. The reverse was true of Pb, Cu and Fe, the sink being the upper part of the B horizon.

1. Introduction

Knowledge of mobility and budgets of metals in forest soils is of great concern to environmental research. The amounts of metals, especially those available in trace quantities, that are cycled through different compartments of the forest ecosystems are still not well known. This knowledge is necessary in estimating cycling rates and long-term effects of metals from atmospheric deposition and in natural soil pools. The prevailing soil acidification (Butzke, 1981; Falkengren-Grerup, 1985; Hallbäck and Tamm, 1985) will increase the release and leachability of many

elements in soil (Norton, 1977; Bergkvist, 1985), those of anthropogenic as well as those of natural origin.

In the biologically most active part of the soil (litter and mor layer), the biological activity has proved to be highly sensitive to heavy metal pollution (Tyler, 1972; 1976a; Rühling and Tyler, 1973). It is necessary to know the metal balances in this horizon to be able to estimate the risk for adverse effects on nutrient mineralization, maybe also on primary productivity.

It is also of great concern to study the loss of metals from the entire soil profile. Ulrich (1975) claimed that there was a risk of increased soil acidification inducing magnesium deficiency in forest trees due to extensive loss from soil of that nutrient. Raisch (1983) found magnesium and zinc deficiency to prevail in five spruce forests in the Black Forest, Southwest FRG (Federal Republic of Germany). There are indications of diminishing nutrient pools in northeast USA (Norton et al., 1980), central Europe (Raisch, 1983) and south Scandinavia (Nilsson, 1985a).

Forest decline is tending to become a widespread phenomenon in Europe (see Breloh and Dieterle, 1985, for the situation in FRG) and in northeast USA (Bruck, 1985). In parts of central Europe nutrient deficiency seems to be a main factor in forest decline (Zöttl, 1985; Zöttl and Huettl, 1985) and fertilization with eg. magnesium improved growth and vigour rapidly.

Soil acidification is also considered to increase soil solution concentration of aluminium and heavy metals to toxic levels for the tree roots (Ulrich, 1983a; Matzner and Murach, 1985). These authors claim that every hypothesis trying to explain the present forest decline must include root decline as a major symptom. When spruce seedlings were grown at aluminium concentrations comparable to those found on several occasions in soil solutions of this study, root and shoot growth declined significantly (Rost-Siebert, 1983; Hutchinson et al., 1985). Allium exposed to solutions from the A horizon of the Värnsjö soil reported in this paper showed a marked decrease in root elongation as aluminium concentration in soil solution increased. In the B horizon soil solution with a high aluminium content (5-15 mg l⁻¹) no root growth at all was observed (Berggren and Fiskesjö, pers. comm.).

The objectives of this study on spruce forest ecosystems are to: a) quantify the deposition and biomass cycling of metals (sodium, potassium, magnesium, calcium, iron, manganese, aluminium, copper, zinc, cadmium, lead, chromium and nickel) and hydrogen ions; b) quantify the net loss of metals; c) quantify metal budgets in different soil horizons; d) study the differences in concentration of metals, hydrogen and soluble organic compounds in soil solution from the various soil horizons; e) study the release and re-precipitation of organic compounds in the soil.

2. Site Description

The two areas studied are mature mixed-coniferous forests situated in southwest Sweden. Their main tree species is Norway spruce (*Picea abies*); some Scots pine (*Pinus sylvestris*) also occurs, but it does not influence the studied plots.

The southern study area (Värsjö) is situated 130 km NNE Lund, south Sweden. The mature stand is mainly even-aged, the spruce being ca. 80 yr, younger trees occurring in openings. The vegetation of the forest floor is patchy. Areas dominated by the grass *Deschampsia flexuosa* alternate with areas dominated by the dwarfshrub *Vaccinium myrtillus*, the mosses *Ptilium crista-castrensis* and *Pleurozium schreberi* or areas devoid of vegetation surrounding the tree stems. No shrub layer is usually present.

The stand is developed on a low hill of sandy glacial till, originating from siliceous rocks, poor in carbonates. It is partly surrounded by mires. The soil is generally very deep and freely drained. Arable land is absent within several km of the study area. The soil is an iron podzol, with a 7-10 cm purely organic litter+mor horizon (A₀+A₁), a 5-12 cm greyish mineral horizon (A₂), and a 25-35 cm illuvial horizon (B). The vertical distribution of organic matter, clay content and pH of the soil profile are shown in Table I.

TABLE I

Content of organic carbon and clay (percent of the dry weight), pH-H₂O and pH-KCl of the two studied soils at Värsjö and Gårdsjön. Sampling period: Sept at Värsjö and April at Gårdsjön.

Soil horizon	Soil depth cm	Organic carbon		Clay		pH-H ₂ O		pH-KCl	
		Värsjö	Gårdsjön	Värsjö	Gårdsjön	Värsjö	Gårdsjön	Värsjö	Gårdsjön
A ₀₀ +A ₀	0-5	48	50	1.1	0.9	3.6	3.7	2.8	2.8
A ₁ +A ₂	5-15	9	18	1.6	1.8	3.8	3.9	3.0	3.1
B ₁	15-35	2.9	5.3	1.0	1.8	4.2	4.3	4.0	4.0
B ₂	35-55	1.8	3.2	0.3	1.4	4.4	4.5	4.4	4.3

The northern study area (Gårdsjön) is situated within the catchment of lake Gårdsjön on the Swedish west coast, c. 40 km N Göteborg. Two microcatchments (3.3 and 3.6 ha), delimited by low hills, are studied. They have a similar vegetation. Norway spruce dominates with Scots pine, though only spruce occurs on the plots

studied. The forest is 70-80 years old. The field and ground layer is mainly dominated by the same dwarf shrubs, mosses and lichens as at Värnsjö. The area as a whole is dominated by mixed coniferous forest alternating with lakes, exposed bedrock and mires. Many hills delimit several microcatchments. The soil is generally very shallow. Depths of 50 cm or less are characteristic of more than 50 percent of the area. An iron-humus podzol is the most common soil type, but an iron podzol with less organic matter in the B horizon can be found on top of the hills. A distinct C horizon is often lacking, the lower part of the B horizon being in direct contact with the bedrock. The texture is dominated by fine sand and silt (Olsson et al., 1985). The depths of the soil horizons are similar to those of the Värnsjö soil. The content of organic matter and clay, and the pH in different soil horizons, are shown in Table I.

The areas studied were extensively utilized during the 19th century for grazing and, possibly, hay-making. Most of the ground, at least at Värnsjö, was cleared from stones already prior to the 19th century, nowadays evidenced by scattered fences of stone and moss-covered stone-heaps.

In the Värnsjö area no sources of pollutants of any great importance to the deposition of acid or metals occur within 50 km of the area. The area fulfills the demands of a "background" site of southwestern Sweden. In the Gårdsjön area local sources occur. As close as 10 km from the study site, there is a petrochemical industry at Stenungsund. Here, an oil-fired power plant was also in operation some 10 years ago.

3. Climate and Weather Conditions

The influence of the Atlantic gives a maritime climate to the southwest part of Sweden. The most frequent winds are from the southwest. The main part of the precipitation sum of the year falls in late autumn and winter. Mean annual precipitation of the southern study area (Värnsjö) is c. 785 mm according to data from four meteorological stations within 15 km (Elleson, unpublished, pers. comm). In the northern study area (Gårdsjön) the mean annual precipitation sum is 730 mm according to data from four official meteorological stations within 60 km. However, the precipitation is highly influenced by altitude and topography (orographic effect), being 700-1200 mm in the region as a whole. The yearly precipitation sums during the period of investigation (1979-1981 at Värnsjö, 1980-1984 at Gårdsjön) were never below normal (Tables II and III), though differences between seasons were great; part of the summers of 1982, 1983 and 1984 were drier than normal.

TABLE II

Precipitation (mm) in the Värnsjö area, 1979-1981, mean of four adjacent meteorological stations (in brackets calculated as percent of normal values 1965-1974) (Ellesson, pers. comm.).

value Period	1979	1980	1981	Normal 1965/74
Jan-March	209 (140)	89 (60)	268 (180)	149
April-June	144 (86)	194 (115)	160 (95)	168
July-Sept	230 (103)	280 (126)	172 (77)	223
Oct-Dec	259 (106)	486 (198)	394 (161)	245
Jan-Dec	842 (107)	1049 (134)	994 (127)	785

TABLE III

Precipitation (mm) in the Gårdsjö area 1980-1984 (in brackets mean of four adjacent meteorological stations calculated as percent of normal values 1931-1960*).

Period	1980	1981	1982	1983	1984
Meteorological stations:					
Jan-March	(55)	(134)	(118)	(158)	(110)
April-June	(126)	(147)	(107)	(141)	(104)
July-Sept	(116)	(71)	(93)	(79)	(79)
Oct-Dec	(158)	(147)	(164)	(94)	(123)
Jan-Dec	(120)	(120)	(122)	(109)	(103)
At the study site:					
Jan-Dec	1162	1082	1250	1235	975

* According to national meteorological statistics (SMHI)

The years 1979, 1980 and 1981 were cold, yearly mean, summer and winter temperatures being below normal. Warmer than normal were 1982, 1983 and 1984 with warm summers and autumns. The length of the growing season (mean daily air temperature $>6^{\circ}\text{C}$, at least 4 days in succession) ranges between 200 and 210 days in both areas.

The snow cover is not often stable throughout the winter. However, the four winters from 1978/1979 until 1981/1982 were characterized by a considerable snow cover (20-50 cm) of above-normal duration. The other winters during the study were closer to average. In a normal year, the run-off amounts to 300-400 mm, the mean annual evapotranspiration being c. 60 percent of the precipitation sum.

4. Materials and Methods

4.1. INSTALLATION WORK AND FIELD SAMPLING

Lysimeters were constructed in plexiglass; the only other components used were an adhesive and a plastic net, both with insignificant traces of metals. Soil cores from places with freely drained soil were taken vertically from the surface. Steel cylinders of the same length and diameter as the lysimeters were used. The cores were transferred to the lysimeters with a minimum of disturbance and the whole units were replaced in their original positions, after two supporting plastic cylinders had been installed (Fig. 1). Design and installation procedures were originally developed by Tyler (1981) who studied the leaching of several metals from the A horizon below a spruce plantation in southernmost Sweden.

The exact positions were chosen subjectively in such a way that certain criteria were fulfilled: 1) within the crown projection of spruce, 2) no direct influence from other tree species, 3) the ground vegetation as uniform as possible, usually without vegetation or with some mosses, 4) the lysimeters in each set kept as close together as possible.

Four different soil depths were chosen for each set of lysimeters. They represented approximately the $A_{00} + A_0$ horizons, including some moss vegetation (depth 0-5 cm), the A horizon including most of A_2 (depth 0-15 cm), the A horizon + the B_1 horizon (depth 0-35 cm) and finally the A horizon + most of the B horizon including B_2 (depth 0-55 cm).

The diameter of the lysimeters was 290 mm (0-5 and 0-15 cm) or 190 mm (0-35 and 0-55 cm). Two different sets of lysimeters were installed at Värnsjö, and three at Gårdsjön. This makes two and three "replicates", respectively, for each soil depth.

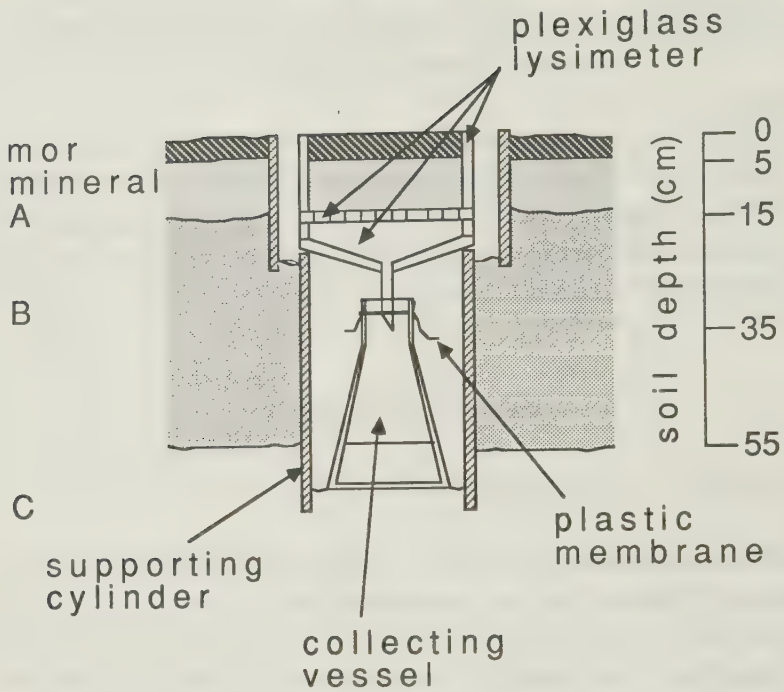


Fig. 1. Lysimeter installation, one of the four soil depths studied (15 cm, A horizon).

The lysimeters at Värnsjö were installed in September 1978 (5, 15 and 35 cm) and in September 1979 (55 cm). Sampling started in October 1978 and 1979, respectively, and ceased in December 1981. The lysimeters at Gårdsjön were installed in April 1980. Sampling started in July 1980 and is at present (Jan 1986) continuing. Precipitation water percolating the soil cores was collected in Erlenmeyer flasks (Duran glass), which were sealed with a plastic membrane, through which the outlet tubes of the lysimeters could easily penetrate.

Open-field precipitation was collected at the Värnsjö site in 4 plastic funnels (diam. 22 cm) placed on a 5 m tall mast, situated on a nearby bog, and connected to plastic bottles on the ground through silicon tubes. Throughfall water in the forest was collected in 10 systematically distributed plastic funnels (diam. 30 cm) connected to plastic bottles. Plastic nets in the bottom of these funnels trapped the

litterfall which was also collected. During winter an equal number of plastic buckets was used (diam. 40 cm and 30 cm for open-field and throughfall, respectively). Polyethylene was used in all plastic equipment.

Percolates obtained and used for measurements and calculations were never turbid. To minimize the risk of the metal concentrations of the percolates being altered by the installation procedure, the first few samples were omitted. The collection interval was about 1 month, shorter during periods of heavy rain and longer during periods when the soil was frozen or too dry. Samples of open-field precipitation, throughfall and litterfall were taken at the same time as the lysimeter percolates.

4.2. SAMPLE PRETREATMENT

All glassware and plastic material was acid cleaned before use. At least one blank in each series of six samples was handled through sample treatment and analysis. Water volume and pH were measured immediately after each collection. A small amount of the percolate was stored at -20 °C for subsequent determination of dissolved organic carbon (DOC). Lysimeter percolates and open-field precipitation samples were treated separately; the throughfall water from each sampling occasion was made into 2 bulk samples. From each sample 1000 ml was taken (except when the amount was smaller) and transferred to a 2 l Erlenmeyer flask. The flask was sealed with a hood of fine-grained filter paper and placed in an evaporation cabinet at 105 °C until dry. The evaporation residue was treated with 10 ml HNO₃ (conc., anal.gr.) for total destruction of organic matter and converting the metals into a chemically uniform and soluble state. Remaining acid was evaporated to c. 2 ml and the digestion residue diluted to 25 ml.

The needle litter from each sampling occasion was made into one bulk sample and dried at 35 °C to constant weight. Total dry weight was determined and 2.5 g were digested in a 250 ml Erlenmyer flask in the same way as described for the evaporation residue. Tree biomass was sampled from 3 different trees at the Gårdsjön site (samples made available by Hallbäcken, Swedish University of Agricultural Sciences, Uppsala). C. 100 samples from different parts of the trees were digested as for the needle litter, and analysed for metals.

Simultaneously with the lysimeter installation, four soil profiles around the lysimeter soil core were sampled at six levels (0-5, 5-15, 15-25, 25-35, 35-45 and 45-55 cm, area of sampling cylinder: 38 cm²). All samples from the same level were pooled into a bulk sample. Total and extractable metal contents were determined.

The total contents of metals in the soil samples were determined by atomic absorption spectrophotometry (see 4.3), after treating 1 g dry wt. of soil with hot

conc. $\text{HNO}_3 : \text{HClO}_4$ (4:1) for three days. Complexible heavy metals (copper, zinc, lead, cadmium, nickel and chromium) were determined after extraction of fresh soil (corresponding to 20 g dry wt.) with 100 ml 0.05 M Na-EDTA, against similarly prepared standards. This is regarded as an approximation of the secondary, non-lattice fractions. Acid ammonium acetate (pH 4.8; 1 M) extractable metals (sodium, potassium, calcium, magnesium, iron, manganese and aluminium) were determined, also against similarly prepared standards, after extraction of fresh soil (corresponding to 20 g dry wt.) with 200 ml of the extractant and subsequent evaporation and digestion of 100 ml of the extract as described for lysimeter solutions above; in this case the digestion residue was diluted to 50 ml. This could be regarded as an approximation of the exchangeable fractions. Soil pH was determined after extraction of fresh soil (corresponding to 5 g dry wt.) with 50 ml extractant, distilled water and 0.2 M KCl solution, respectively.

4.3. SAMPLE ANALYSIS

Thirteen metals were analysed: sodium, potassium, calcium, magnesium, iron, manganese, aluminium, copper, zinc, lead, cadmium, chromium and nickel. Furthermore, pH, organic matter (organic carbon) and clay content of soils were determined.

The following analytical methods were used. Metals were determined by acetylene-air flame atomic absorption spectro-photometry (Varian AA6) with recorder registration, unless otherwise stated: sodium and potassium with 1000 ppm CsCl in solutions; calcium and magnesium with 10 000 ppm LaCl_3 in solutions; iron, manganese, copper, zinc and chromium (Cr with a surplus of acetylene), standard procedure; aluminium by acetylene- N_2O flame; cadmium and lead with H_2 background corrector; nickel by carbon-rod technique with H_2 background corrector and registration with curve area integrator and recorder; dissolved organic carbon (DOC) in lysimeter solutions was determined by infrared technique using a Beckman 915B carbon analyser; pH was determined electrometrically at c. 20 °C, using ca. 10 ml of the untreated waters or settled soil extracts; organic matter in soil samples was determined as percent organic carbon by infrared technique using a LECO CR 12 carbon determinator; percent clay content was determined gravimetrically after sedimentation of soil samples in water and subsequent drying and ignition of subsamples taken after a fixed time interval and at a fixed depth in the water column.

5. Results

5.1. DATA PRESENTATION

Data are presented in the following ways: 1) Yearly means of the concentrations of metals, hydrogen ions and dissolved organic carbon, and pH, of precipitation water, throughfall water, soil solutions from various depths and stream water (run-off); 2) Extractable and "total" amounts of metals in the soils, and (at the Gårdsjön site) metal content in biomass; 3) Metal budgets of ecosystems and soils.

Concentrations in solutions are calculated as mg l^{-1} for DOC, sodium, potassium, calcium, magnesium, iron, manganese and aluminium; as $\mu\text{g l}^{-1}$ for copper, zinc, lead, cadmium, chromium, nickel and hydrogen ions. Metals in soils and biomass are calculated as g m^{-2} ; the flow of metals between the compartments of the ecosystem as $\text{g m}^{-2} \text{ yr}^{-1}$ and $\text{mg m}^{-2} \text{ yr}^{-1}$, respectively.

5.2. GENERAL CONSIDERATIONS OF THE BUDGET CALCULATIONS

The term "ecosystem budget" is used to indicate whether there is a net increase of the metal (positive budget; higher input than output) or a net decrease (negative budget; lower input than output) in the ecosystem as a whole (down to a soil depth of 55 cm). This is shown in Table VII (calculated from data given in Fig.4 for the Värjsjö forest and from Table V for the Gårdsjön forest). The ecosystem budget is considered positive if the wet and the dry deposition together are greater than the outflow below the rooting zone at 55 cm. Correspondingly, the budget is considered negative if the outflow is greater.

Amounts of water collected from the lysimeter soils are over-estimations of the actual situation, due to the use of lysimeter technique (root uptake by the trees is excluded). Therefore, water flows were estimated using a numerical model (Jansson and Halldin, 1980) based on assumed plant and soil properties. Transpiration from the forest was calculated with a Penman combination equation (Monteith, 1965) using a value of 100 s m^{-1} for the surface resistance when soil water tensions were below 400 cm water. At higher tensions a reduction of transpiration took place. Soil properties, the water retention curve and the unsaturated conductivity function, were roughly estimated from given textural composition. Driving variables to the model, air temperature, vapour pressure, wind speed and cloudiness, were taken from official national meteorological statistics (SMHI). In addition the most important driving variable, precipitation, was selected from a denser network of meteorological stations (Elleson, pers. comm.). Flux of water used in the calculations of the soil flux of metals at Värjsjö was the simulated amounts of run-off water for the forest

(precipitation at the four adjacent stations during 1980-1981 used in the model: 950-1050 mm yr⁻¹; run off ("percolation") from the model: 470 mm yr⁻¹). At Gårdsjön the run-off measured in the microcatchments was used in the metal flux calculations of the soil at this site (precipitation in the study area during July 1980 - Sep 1984: c. 1200 mm yr⁻¹; run-off ("percolation"): 623 mm yr⁻¹). Data on run-off were obtained from another project (Johansson and Nilsson, 1985) for those microcatchments where the lysimeters were installed. In Fig. 4 and Table V the flux of metals in the soils were calculated using run-off values.

5.3. CHEMICAL COMPOSITION OF THE WATER ON ITS WAY THROUGH THE ECOSYSTEM

Quite different concentrations of most metals were measured in open-field precipitation and in throughfall water, throughfall concentrations being higher, as a rule. The contribution from the tree crowns was considerable, in particular of manganese, potassium, magnesium and calcium (Fig. 2). These elements have a rapid ecosystem cycling and/or a large proportion of dry deposition. Also certain heavy metals show significant augmentation from open-field precipitation to throughfall; zinc and cadmium are two good examples of this pattern. However, lead concentrations increase only slightly on the passage through the canopy. The throughfall water was also enriched in hydrogen ions compared to precipitation; the lowest pH of the water in the system was usually found in the throughfall. The yearly mean pH at Värnsjö of open-field precipitation was 4.20, of throughfall 3.68; at Gårdsjön these figures were c. 4.37 and 3.96, respectively, as calculated from Grennfelt et al. (1985).

When the throughfall water reached the soil surface and percolated the soil, the solution chemistry was, again, greatly altered. This is reflected by the change both in pH and in the contents of metals and dissolved organic carbon (DOC). The organic topsoil (upper 5 cm litter and mor layer) made the solution pH increase considerably. The yearly mean pH at Värnsjö and Gårdsjön in soil solution at 5 cm was 4.03 and 4.09, respectively (Figs. 2-3).

At Värnsjö the lowest soil solution pH was usually measured after passage of the organic horizon, and at Gårdsjön after passage of the mineral part of the A horizon, at 15 cm soil depth (mean pH 4.14 and 4.00 at Värnsjö and Gårdsjön, respectively). The content of organic acids was here at its highest level. In the B₁ horizon, at 35 cm, the pH had increased (pH 4.27 and 4.34 at Värnsjö and Gårdsjön, respectively); no significant increase was found after passage of the B₂ horizon, and the soil solution entering the C horizon must be considered unexpectedly acid (pH 4.23 and 4.45 at Värnsjö and Gårdsjön, respectively).

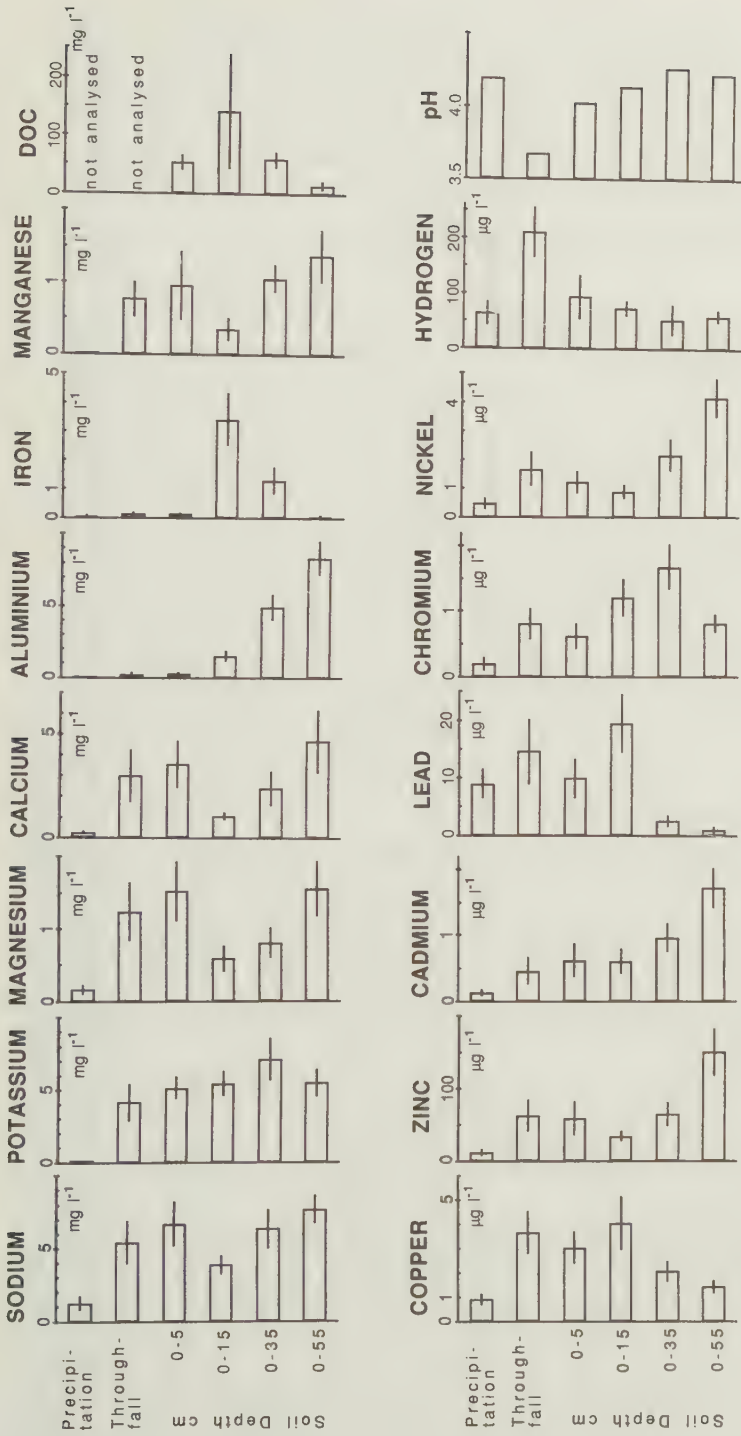


Fig. 2. pH, concentration of metals, DOC (dissolved organic carbon) and hydrogen in precipitation, throughfall and soil solutions from different depths at Värnsjö. Means from two years (1980 - 1981) and 95 percent confidence limits; n=19 (precipitation and throughfall) or 44 (soil solution).

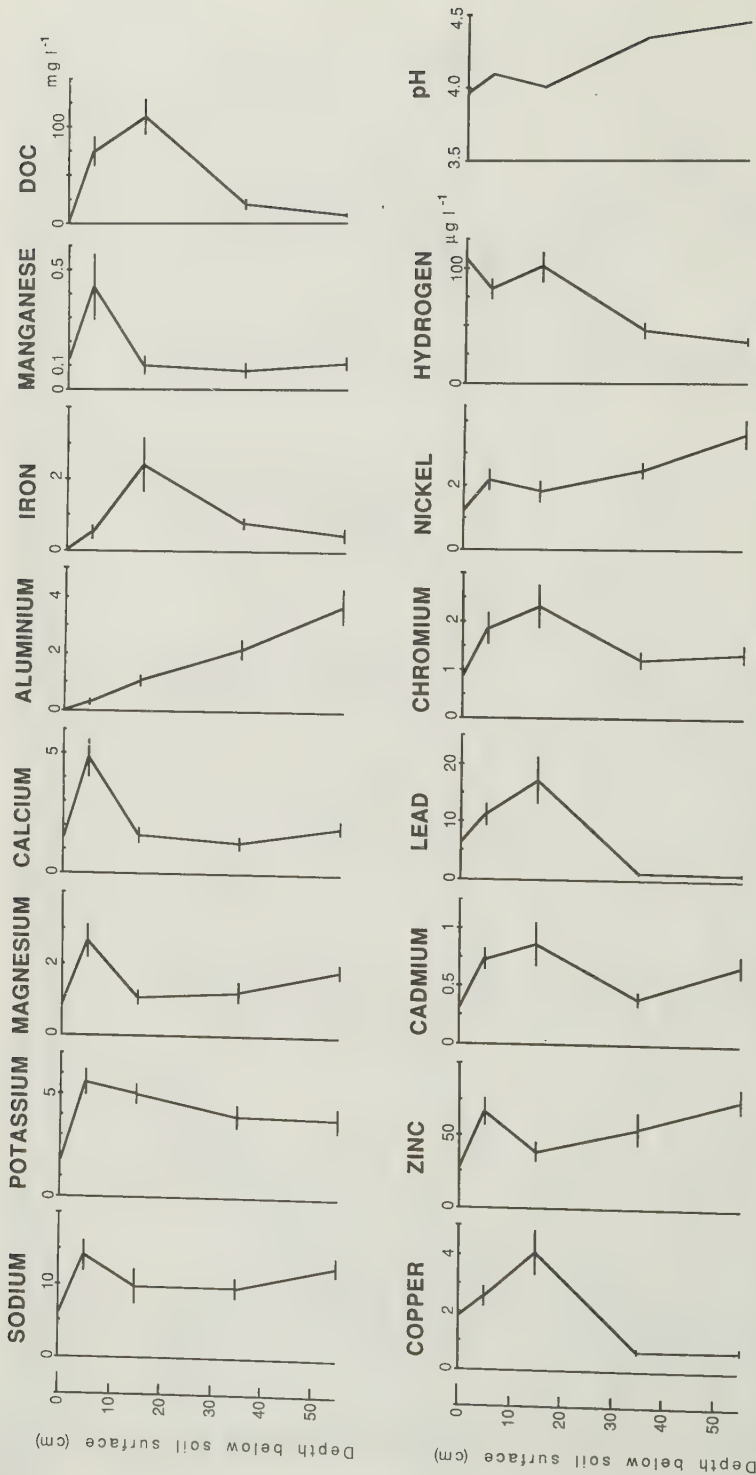


Fig. 3. pH, concentration of metals, DOC (dissolved organic carbon) and hydrogen in throughfall (=0 cm depth) and soil solution at different depths at Gårdsjön. Throughfall data calculated from Grahn and Rosén (1983), Grennfelt et al. (1985) and Hultberg (1985). Means from four year (1980 - 1984) and 95 percent confidence limits for soil solution, $n=90$.

The release of dissolved organic matter is considerable in the A horizon; at 15 cm soil depth the content as DOC of the soil solution is at its peak, 100-150 mg l⁻¹ as yearly means. As the very dark brown-coloured soil solution from the A horizon percolated the B horizon it became increasingly less brown-coloured. Most of the dissolved organic matter precipitated in the upper part of the B horizon (Figs. 2-3). At 55 cm (lower B₂) very little organic matter was left in the solution, which was visibly uncoloured at this soil depth; the content of DOC was still 10 to 15 mg l⁻¹, however.

Together with the organic matter almost all lead and iron disappeared from the solution in the B horizon, and so did part of the copper and chromium. Organic species of aluminium also precipitated in the upper part of the B horizon together with the organic matter (Nilsson and Bergkvist 1983). Aluminium in soil solutions from the lower B horizon originates mainly from the mineral soil of this horizon and c. 80 percent of this is an inorganic species.

The concentrations of aluminium, nickel and zinc continued to increase in the soil solution at least throughout the whole B horizon. At the Värslö site this was also true of magnesium, calcium, manganese and cadmium. At the Gårdsjön site, soil solution content of magnesium, calcium and manganese decreased through the A and B₁ horizons (down to 35 cm soil depth), but in B₂ (0-55 cm) these concentrations increased again, as was the case with cadmium after an irregular pattern above in the soil. No data are available from the C horizon (below 55 cm).

The contents of metals in the small brook draining the study area at Värslö were also measured during one year (Sept 1980 - Oct 1981) (Table. IV). The stream water was always coloured brown by organic matter (however, no determination of the organic matter content was made). The contents of metals in run-off waters from the microcatchments of lake Gårdsjön, in ground water and in the lake itself are also listed. There is little change in the soil solution content of sodium, calcium, magnesium, copper, chromium and lead leaving the soil profile at 55 cm (Figs. 2-3) on the way to the brook (Table. IV); this is also the case for manganese and iron at the Gårdsjön site. In contrast, at Värslö only about 10 percent of the content of potassium, manganese, zinc, cadmium and nickel was found in the brook compared to soil water concentrations at 55 cm depth; of aluminium only 5 percent. The elimination of these elements from the percolation water thus seems to take place mainly below 55 cm depth. The only significant increase in concentration between the lower B horizon and the brook at Värslö was found for iron.

Table IV

Annual mean of metal concentrations and pH in brook waters, ground water and lake water (lake Gårdsjön). $\pm$ 95 percent confidence limit in waters from the Värnsjö site; n=8.

	Värnsjö: brook	ground water	Gårdsjön: * brook	lake
pH	3.90 $\pm$ 0.08	-	4.15	-
DOC (mg l ⁻¹)	-	-	8.2	-
Na	5.97 $\pm$ 0.96	-	6.8	5.6
K	0.65 $\pm$ 0.17	-	0.61	0.61
Mg	1.81 $\pm$ 0.24	-	1.4	1.2
Ca	4.04 $\pm$ 0.91	-	1.3	1.7
Al	0.37 $\pm$ 0.03	1.7	0.8	0.3
Fe	1.71 $\pm$ 0.92	0.09	0.30	0.06
Mn	0.12 $\pm$ 0.07	0.07	0.06	0.14
Zn (μ g l ⁻¹)	16.1 $\pm$ 2.77	33	21	16
Cu	1.18 $\pm$ 0.29	2.8	0.6	0.6
Cd	0.2 $\pm$ 0.06	0.2	0.2	0.1
Pb	1.19 $\pm$ 0.53	3.1	0.7	1.4
Cr	0.53 $\pm$ 0.28	1.1	0.6	0.2
Ni	0.49 $\pm$ 0.11	1.9	1.0	1.3

* From Grahn and Rosén (1983) except Na, K, Ca, Mg from Hultberg (1985) and pH and DOC from Persson and Broberg (1985).

At the Gårdsjön site about 15 to 25 percent of the soil solution content at 55 cm of potassium, aluminium, zinc, cadmium and nickel was found in the run-off water draining the microcatchments. In the lake water only aluminium, iron, zinc, cadmium and chromium concentrations were significantly lowered compared to run-off. Manganese and lead concentrations were higher in the lake; the concentrations of sodium, potassium, magnesium, calcium, copper and nickel did not differ between the brook and the lake.

5.4. ELEMENT DEPOSITION AND CYCLING

The mean annual input of metals with wet and dry deposition, canopy release, throughfall, litterfall, root uptake (only internal circulation) and loss of metals with percolation water during two years are calculated for the Värnsjö forest (Fig. 4). Mean annual loss of metals with the percolation water is calculated for the Gårdsjön site, the measurement period being four years. Soil fluxes are compared with input by wet and dry deposition and throughfall as well as litterfall and accumulation in biomass (Table V). Extractable and "total" contents of metals in the soil at the two

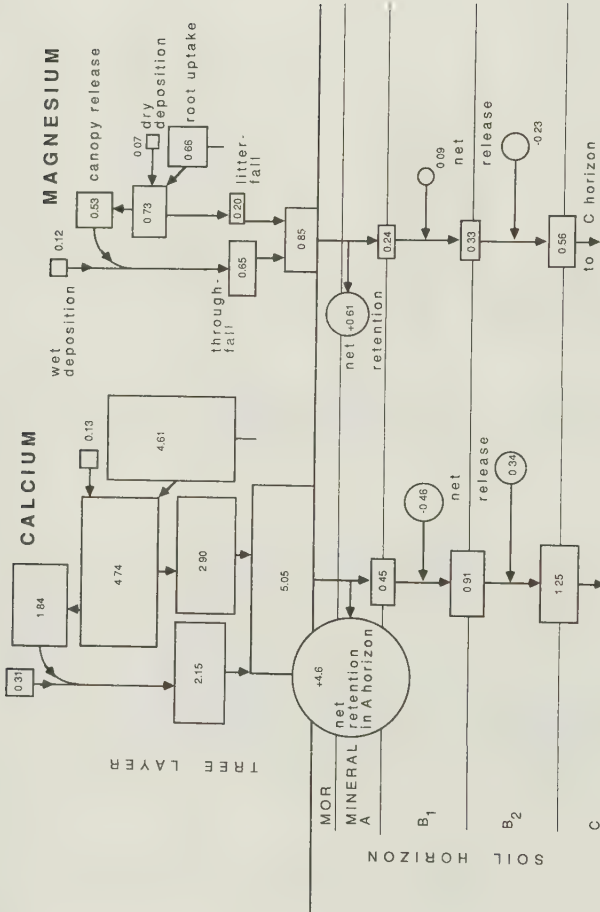


Fig. 4b.

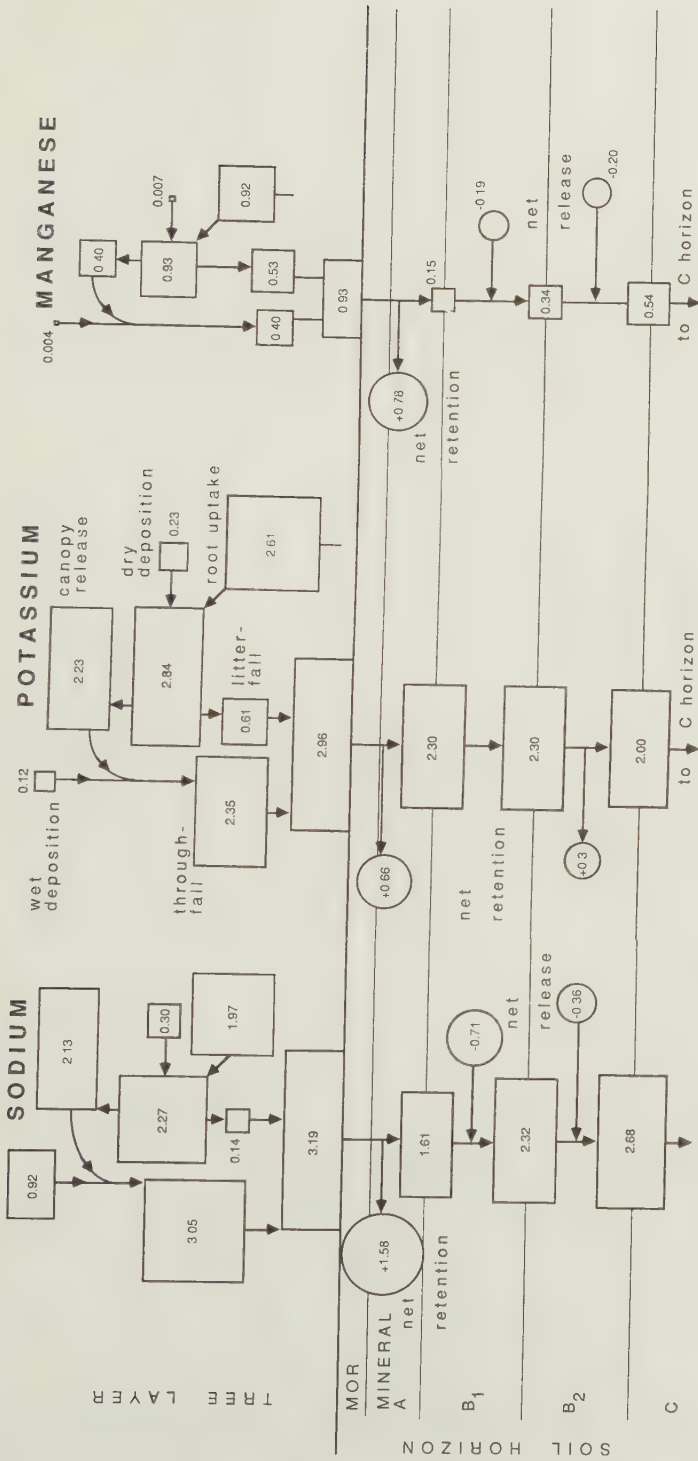


Fig. 4c.

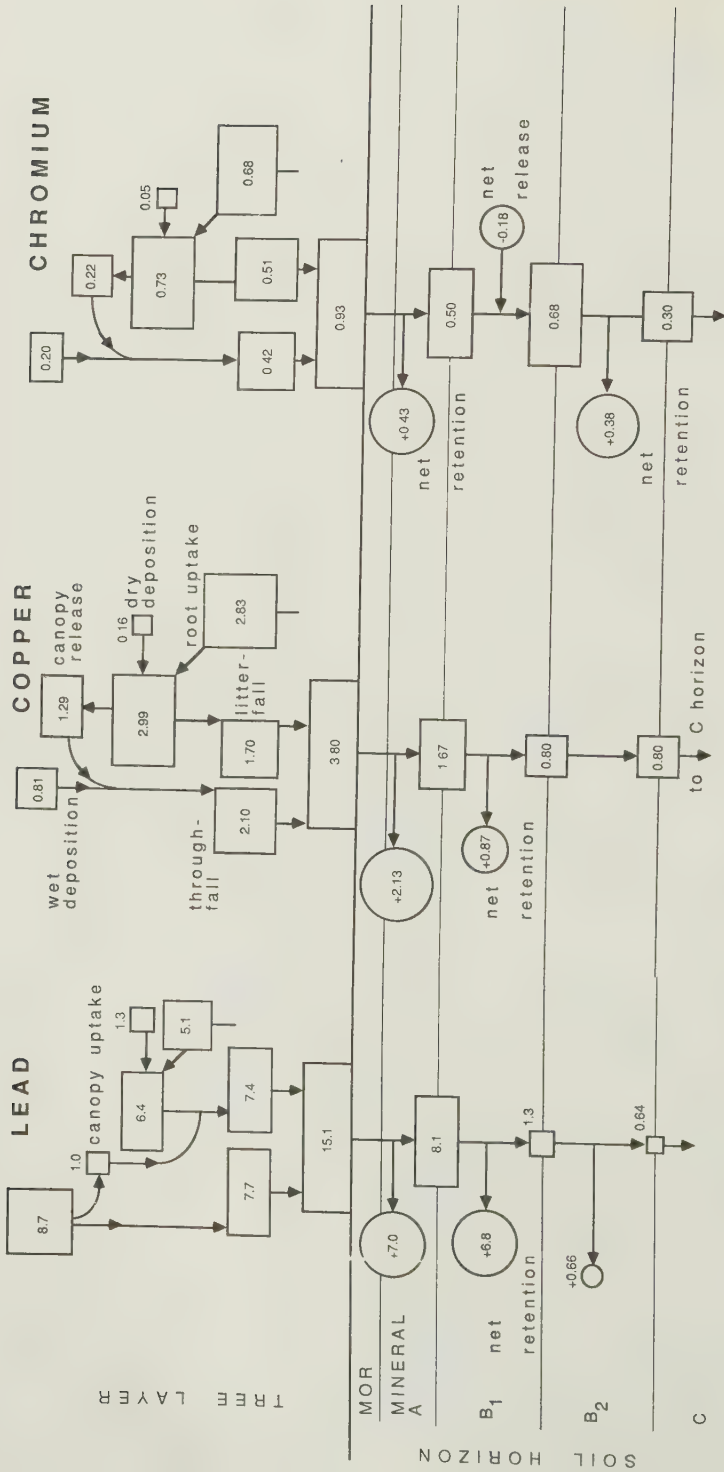


Fig. 4d.

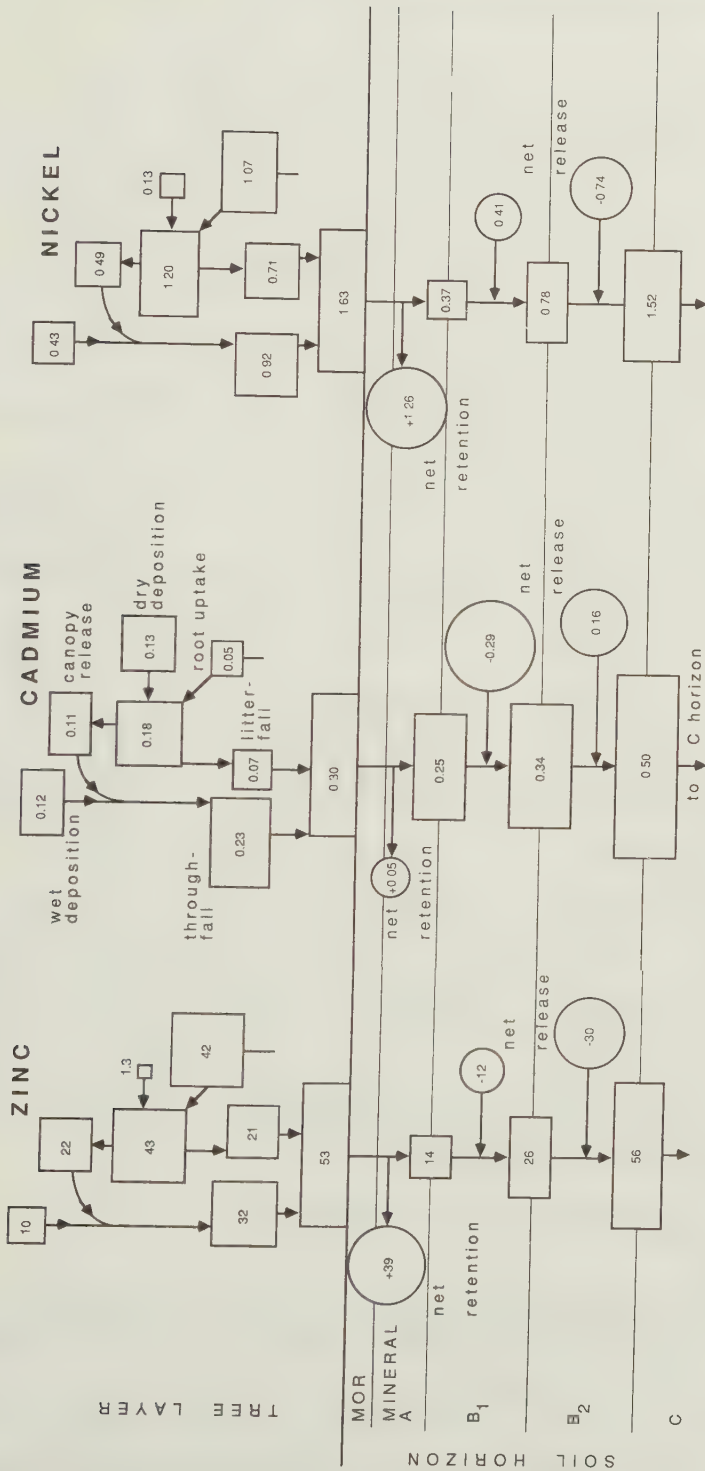


Fig. 4e.

sites have been calculated, and at Gårdsjön also the biomass content of metals (Table VI).

The importance of "wet" deposition (with precipitation funnels) to the ecosystem flux differs greatly among the metals (Fig. 4 and Table V). Of the gross input of manganese to the forest floor (= throughfall + litterfall) in the spruce forest ecosystems, the contribution from precipitation was almost negligible. Also the supply of potassium and calcium from precipitation was very small, only a few percent of the amounts reaching the soil surface during a year.

The contributions from wet deposition to the forest floor of sodium, magnesium and aluminium as well as of iron, nickel, copper, zinc (at Värjsjö) and chromium are somewhat greater, about ten to thirty percent of the gross input to the forest floor. Of lead and cadmium roughly fifty percent of the gross input is supplied in wet deposition, this being also true of zinc at Gårdsjön.

The dry deposition of several metals to the Värjsjö spruce forest was studied by Wiman (1984; 1985). Dry deposition values in Fig. 4 are yearly estimates from model-generated mean deposition rate over the first 850 m from upwind forest edge and inwards (Wiman, 1984 and pers. comm.) The dry deposition of potassium and manganese was twice as high as the wet deposition, while the dry deposition of calcium was only about half of the wet deposition. The sum of dry and wet deposition of these metals was not sufficient to explain the gross input to the soil surface. Thus, cycling between soil and vegetation is of great importance to the ecosystem budget of these metals. The wet deposition of chromium, lead, nickel, zinc and copper dominated over dry deposition, whereas the wet deposition of iron was only half of it.

The Värjsjö dry deposition estimations in Fig. 4 were used also at Gårdsjön (Table V), except sodium and magnesium from the Gårdsjön site (Grennfelt et al. 1985). The deposition rate of at least these two metals was much higher at Gårdsjön due to the greater maritime influence there. However, in estimations of ecosystem budgets for the Gårdsjön forest, values on dry deposition at Värjsjö may be used, as the structure and density of the two forests are comparable, though anthropogenic and maritime influences on air masses differ.

5.5. SOIL BUDGETS

Most metals, except iron and aluminium, are to some extent accumulated in the A horizon of Värjsjö (Fig. 4). The A horizon at Gårdsjön is losing iron, aluminium, sodium, chromium and cadmium (Table V).

There is a net release of several metals from the B horizon at the two sites. This is true for sodium, manganese, magnesium, calcium, aluminium, zinc, nickel and

Table V

Fluxes of metals (annual means) in different compartments of the Gårdsjön forest. Output from different soil horizons $\pm 95\%$ confidence limits; $n=12$ (3 lysimeters at each soil depth $\times 4$ years).

Deposition:				Soil solutions from (depth):				Acc. in biomass:	
	Wet*	Dry**	Total	Through-fall*	15 cm	35 cm	55 cm	(excl yr shoots + needles)	yr shoots + needles "litterfall"
$(\text{g m}^{-2} \text{ yr}^{-1})$									
Na	0.85	3.2	4.05	4.29	6.01 $\pm$ 2.17	5.57 $\pm$ 0.91	7.67 $\pm$ 1.03	0.08	0.11
K	0.06	0.23	0.29	1.29	2.75 $\pm$ 0.76	2.10 $\pm$ 0.41	2.16 $\pm$ 0.70	0.53	1.47
Mg	0.12	0.52	0.64	0.66	0.78 $\pm$ 0.33	0.78 $\pm$ 0.34	1.15 $\pm$ 0.20	0.18	0.39
Ca	0.17	0.13	0.30	1.02	0.97 $\pm$ 0.25	0.84 $\pm$ 0.30	1.15 $\pm$ 0.95	0.88	1.3
Al	0.02	0.20	0.22	0.05	0.56 $\pm$ 0.14	1.25 $\pm$ 0.46	2.15 $\pm$ 0.61	0.11	0.03
Fe	0.02	0.13	0.15	0.03	0.35 $\pm$ 0.17	0.24 $\pm$ 0.09	0.14 $\pm$ 0.16	0.09	0.02
Mn	0.002	0.007	0.009	0.09	0.06 $\pm$ 0.04	0.04 $\pm$ 0.01	0.07 $\pm$ 0.03	0.08	0.23
$(\text{mg m}^{-2} \text{ yr}^{-1})$									
Zn	31.8	1.3	33.1	28.3	21.0 $\pm$ 5.56	39.3 $\pm$ 15.9	45.6 $\pm$ 5.61	27	23
Cu	0.74	0.16	0.90	1.3	2.35 $\pm$ 1.25	0.56 $\pm$ 0.29	0.48 $\pm$ 0.11	1.3	1.2
Cd	0.19	0.13	0.32	0.22	0.45 $\pm$ 0.17	0.24 $\pm$ 0.11	0.42 $\pm$ 0.13	0.15	0.05
Pb	6.42	1.3	7.7	4.9	7.62 $\pm$ 2.95	1.12 $\pm$ 0.73	0.24 $\pm$ 0.11	3.4	0.9
Cr	0.25	0.05	0.3	0.65	1.10 $\pm$ 0.41	0.69 $\pm$ 0.28	0.83 $\pm$ 0.29	0.81	0.19
Ni	0.44	0.13	0.57	0.85	1.00 $\pm$ 0.27	1.48 $\pm$ 0.34	2.18 $\pm$ 0.63	1.4	0.8

* Na, K, Mg and Ca (Oct 1980 - Sept 1981) from Grennfelt et al (1985); Fe, Mn, Al, Cu, Zn, Pb, Cd, Cr and Ni (Oct 1980 - Sept 1981) from Grahn and Rosén (1983).

** From Wiman (1984 and pers. comm.), except: Na and Mg, from Grennfelt et al. (1985).

cadmium. These metals have a negative budget in the entire mineral soil (15-55 cm), except cadmium at Gårdsjön where input and output were of the same size (Fig. 4, Tables V and VII). The only metal with a net outflow throughout the A and the B horizons of the two sites was aluminium.

The net fluxes in the soil are usually of the same magnitude at the two sites (Table VII). Aluminium is outstanding with an annual net loss from the entire soil profile amounting to c. 10 percent of the currently exchangeable soil store. The loss of potassium is probably over-estimated by the use of the lysimeter technique. If the rapid root uptake for internal circulation indicated in Fig. 4 and Table V were considered, the net flux of potassium from the soil would probably be reduced.

The spruce forest ecosystem at Värnsjö is losing sodium, potassium, magnesium, calcium, manganese, aluminium, zinc, cadmium and nickel (negative ecosystem budgets) (Fig. 4 and Table VII); the soil release below the rooting zone exceeds the input by wet + dry deposition. Almost at balance is chromium, whereas iron, lead and copper are accumulating in the forest. Sodium, potassium, magnesium, calcium, aluminium, zinc, cadmium, chromium and nickel are being lost from the ecosystem at Gårdsjön. A tendency to balance is encountered for iron and manganese, whereas lead and copper are accumulating (Tables V and VII). Only insignificant amounts of lead (and iron) leave the rooting zone.

6. Seasonal Soil Patterns

The seasonal and annual variability of metal concentrations in the soil solutions of different horizons at Gårdsjön was shown in two earlier papers (Bergkvist, 1983; Nilsson and Bergkvist, 1983); in another paper (Tyler, 1981) the variability in the A horizon was shown for a spruce forest soil within 50 km of Värnsjö. Great differences between seasons are characteristic of most variables studied, though seasonal variability roughly follows the same pattern in different years. Sometimes there is a time lag in the variation of metal concentrations between soil horizons, but most often the seasonal variability between horizons is less regular (even within the same lysimeter set).

As a functional approach, two different seasonal patterns could roughly be distinguished. One group of metals has a concentration maximum during late summer and autumn; iron, aluminium, nickel, chromium, copper and lead fit into this pattern. The same period also shows the maximum peak in the A horizon for dissolved organic matter, several hundred mg l⁻¹ (as DOC) in September. These elements have a pronounced minimum during the winter, when temperature and biological activity in the soil are low.

TABLE VI

Content of metals in the Vårsjö soil and the Gårdsjön biomass and soil, g m⁻²

Soil depth cm	Na	K	Mg	Ca	Al	Fe	Mn	Cu	Zn	Cd	Pb	Cr	Ni
VÄRSJÖ:													
Acid digestible ("total")													
0-5	5	5	11	53	44	74	6	0.23	1.1	-	2.3	0.09	0.07
5-15	32	36	70	242	492	1260	28	0.22	2.5	-	2.1	0.3	0.13
15-35	60	106	232	674	3040	5010	87	0.60	6.7	-	2.9	1.2	0.45
35-55	115	228	526	1290	4830	5810	126	0.85	9.3	-	1.8	2.0	1.5
Σ SOIL 0-55	212	375	839	2260	8410	12200	247	1.90	19.6	-	9.1	3.6	2.2
Extractable*													
0-5	1.0	7.5	3.7	10	0.2	0.2	0.3	0.04	0.8	0.007	1.7	0.011	0.04
5-15	2.3	3.8	2.9	18	9	2.9	1.7	0.03	1.4	0.009	1.7	0.006	0.03
15-35	1.9	4.7	1.4	4.8	96	12	0.7	0.04	1.3	0.009	1.3	0.012	0.05
35-55	2.3	3.3	1.6	3.2	110	3.7	0.3	0.02	0.6	0.007	0.2	0.005	0.07
Σ SOIL 0-55	7.5	19	9.6	36	215	19	3.0	0.13	4.1	0.032	4.9	0.034	0.19
GÅRDSJÖN:													
Σ BIOMASS													
Acid digestible ("total")													
0-5	6	16	12	206	33	38	2	0.2	1.2	-	1.9	0.24	0.09
5-15	34	50	67	400	579	741	9	0.3	4.2	-	2.9	0.40	0.16
15-35	121	309	437	1530	5530	7360	45	0.9	7.6	-	3.6	2.29	1.03
35-55	93	421	750	162	7340	6630	67	1.2	11.5	-	2.0	3.30	1.94
Σ SOIL 0-55	254	796	1270	2300	13500	14800	123	2.6	24.4	-	10.4	6.23	3.22
Extractable*													
0-5	4.3	7.8	6.9	13	0.4	0.1	1.1	0.04	0.7	0.009	1.5	0.009	0.04
5-15	5.7	6.7	8.6	46	8	1.5	0.6	0.05	1.1	0.02	2.0	0.01	0.05
15-35	7.2	7.1	1.7	3.7	140	22	0.1	0.06	1.9	0.01	0.9	0.03	0.07
35-55	5.5	6.4	0.5	2.9	160	4.2	0.1	0.04	1.6	0.006	0.3	0.01	0.06
Σ SOIL 0-55	22.7	28.0	17.7	66	308	28	1.9	0.19	5.3	0.05	4.7	0.06	0.22

* Na-EDTA: Cu, Zn, Cd, Pb, Cr, Ni; Acid NH₄Ac: Na, K, Mg, Ca, Al, Fe, Mn

The second seasonal pattern is characterized by maxima during the winter. This is demonstrated by sodium, magnesium and calcium; potassium, manganese, zinc and cadmium seem to fit into both groups.

Hydrogen behaves differently in the various soil horizons. Soil solution pH in the mor layer is strongly influenced by the composition of precipitation; eg., snow-melt gives a pronounced pH-minimum. If the soil solution is collected from the lower A horizon, the pH-minimum is, instead, found in August - October. At the same time the maximum concentration of DOC is found. As an average, seasonal patterns in the B horizon are not quite as evident as in the A horizon.

7. Discussion

7.1. SOIL PROCESSES

It is evident from the study that the leachability in the soil differs greatly among metals. Generally, the metals demonstrate two distinct patterns of metal release from the spruce forest soils. As the organic matter in the mor layer is mineralized there is a release of soluble organic acids. These are transported through the A horizon with the percolating soil water. Iron, aluminium, lead, copper and chromium are known to form stable complexes with dissolved organic acids (Himes and Barber, 1957; Stevenson, 1972, 1975, 1976; Verloo et al., 1973; Cheshire et al., 1977; Kirkham, 1977), and are transported through the soil in complexed form. The amounts of these metals released from the A horizon are mainly regulated by the dissolution of organic matter, as shown by Tyler (1981). A high biological activity in the mor layer favours the formation of dissolved organic acids and the release of these metals from soil. Maximum release was found in late summer and autumn, at high soil temperature and soil moisture.

This vertical transport of metal-organic complexes is a normal feature of the podzolization process. It is described as an acid dissolution of hydroxides and silicates of aluminium and iron and a subsequent complex formation between these metals and dissolved organic acids. The dissolved complexes are believed to become gradually saturated by metals and to precipitate at zero charge (see eg. Petersen, 1976). As complexes many trace elements are transported in the soil with an organic iron-aluminium complex and may be co-precipitated with this (Mitchell, 1964; Gomah and Sakhar, 1972; Bolter, 1974). Most of the organic matter, iron, lead, copper and chromium released from the A horizon was accumulated in the upper part of the B horizon.

TABLE VII

Annual metal budgets of the two forests (in brackets the change in the soil pool of metals as percent of current extractable amounts), "+" denotes an increase (gain) and "-" a decrease (loss). (Calculated from Fig. 4 and Tables V and VI, no biomass accumulation assumed.)

	Mineral soil (B horizon)*			Ecosystem budget**		Catchment study at Gårdsjön***
	Värsjö	Gårdsjön	Värsjö	Gårdsjön		
(g m ⁻² yr ⁻¹)						
Na	-1.1 (25)	-1.7 (13)	-1.46 (19)	-3.6 (16)		-0.14
K	+0.30 (4)	+0.59 (4)	-1.7 (7)	-1.9 (7)		+0.24
Mg	-0.32 (11)	-0.37 (17)	-0.37 (4)	-0.51 (3)		-0.32
Ca	-0.80 (10)	-0.18 (3)	-0.81 (2)	-0.85 (1)		±0
Al	-2.5 (1)	-1.6 (0.5)	-2.9 (1)	-1.93 (0.6)		-0.53
Fe	+1.4 (9)	+0.21 (0.8)	+0.14 (0.7)	+0.01 (0.04)		-0.17
Mn	-0.39 (39)	-0.01 (5)	-0.53 (18)	-0.06 (3)		-0.04
(mg m ⁻² yr ⁻¹)						
Zn	-42 (2)	-18 (0.5)	-45 (1.1)	-13 (0.2)		+16
Cu	+0.87 (1.5)	+1.9 (1.9)	+0.17 (0.1)	+0.42 (0.2)		+0.43
Cd	-0.25 (2)	+0.03 (0.2)	-0.25 (0.8)	-0.10 (0.2)		+0.09
Pb	+7.5 (0.5)	+7.4 (0.6)	+9.4 (0.2)	+7.5 (0.2)		+6.0
Cr	+0.20 (1)	+0.27 (0.7)	-0.05 (0.1)	-0.53 (0.9)		-0.06
Ni	-1.2 (1)	-1.2 (0.9)	-0.96 (0.5)	-1.6 (0.7)		-0.18

* Input to 15 cm minus output from 55 cm soil depth.

** Total deposition (wet + dry) to the forest canopy minus output from 55 cm soil depth.

*** From Hultberg (1985) (Na, K, Mg, Ca) and Grahn and Rosén (1983) (Al, Fe, Mn, Zn, Cu, Cd, Pb, Cr, Ni).

Soil solution content of aluminium increases continuously through the B horizon, though this element would be expected to precipitate in the upper B horizon according to podzolization theory. In an earlier paper (Nilsson and Bergkvist, 1983) this was explained by the occurrence of at least two different aluminium species. Aluminium in the A horizon is almost totally organic; this species disappears gradually from the solution with depth as the soluble organic matter precipitates. Instead, an inorganic aluminium species appears and increases in concentration downward through the B horizon, constituting more than 80 percent of total aluminium at the transition to the C horizon. The observed high concentrations of mainly inorganic aluminium in soil solution (more than 40 mg l⁻¹ on occasions) were claimed to be at least partly due to a high atmospheric deposition load of acidifying substances, where acid sulphur compounds are one important constituent.

A constantly quite high soil solution acidity through the B horizon was shown in the study. Regulation of soil solution acidity was explained by the vertical distribution of DOC and the two aluminium forms (Nilsson and Bergkvist, 1983). Using hydrogen ions as the dependent variable in a linear regression, DOC was the best predictor of soil acidity in the mor layer, organic aluminium species in the mineral A horizon and inorganic aluminium in the lower B horizon. Thus, acidity in the A horizon is likely to be regulated mainly by biological activity together with ion exchange and direct protolysis of dissolved organic acids; in the deep B horizon hydrolysis of aluminium is the main hydrogen ion regulating process (cf. also Ulrich, 1983b).

Soil solution from the deep B horizon contains only minor, though still appreciable, amounts of organic acids. Precipitation of the organic complexes requires dissolution of sufficient metals to cause a neutralization of the negative charge carried by the organic molecules. However, as podzolization proceeds, available iron and aluminium will be removed from the upper soil layers, causing the B horizon to descend gradually. According to Petersen (1980), an increased removal of aluminium from the soil profile, as demonstrated in this paper, would favour the mobilization of organic compounds and hamper their deposition in the B horizon. Thus, one result might be an increased production of water-soluble organic compounds in the upper horizon and a leaching of these to greater depth before precipitation takes place. Petersen (1980) regards this as an amplification of podzolization, induced by increased soil acidity. Some organic compounds probably require larger amounts of metals to become precipitated, and may even be leached out of the soil profile. When A horizon soil solutions from the Värnsjö soil were leached through an anion-exchange resin (DEAE-Sephacel, Pharmacia; method described by Miles et al., 1983) c. 10 percent of the soluble organic compounds was not

recovered (Berggren, pers. comm.), indicating these compounds to be either neutral or to have a positive or only weak negative charge.

The pattern of a gradual release of metals from the mineral soil and an increase in soil solution content of metals through the B horizon was characteristic for aluminium, magnesium, calcium, manganese, cadmium, zinc and nickel; it was less characteristic for potassium. These metals are very susceptible to changes in soil acidity, as demonstrated by experimental acidification of lysimeter soils from the Värnsjö forest (Bergkvist, 1985). The influence of accelerated soil acidification on the increased leachability of these metals is also shown in other studies (for references see Bergkvist, 1985). Even minor pH decreases in added extraction solutions increased the leaching of zinc, cadmium, nickel and manganese significantly from both metal-polluted and unpolluted mor layers according to a laboratory study (Tyler, 1978). These metals are readily extracted from soils by ion exchange (Andersson, 1977).

Ion exchange was thought to be one of the factors determining the calcium and magnesium concentrations in the B horizon soil solution, a probable second factor being mineral weathering (Nilsson and Bergkvist, 1983). Increased disintegration rates of organic complexes or chelates probably increase the solubility of many metals on soil acidification. It is known that many metal-organic complexes become less stable and more soluble at a low soil pH (Schnitzer, 1968; 1969; Massey, 1972). However, complexes of copper and lead with humic substances are characterized by a very high stability, those of manganese, cadmium and zinc by a comparatively low stability (Schnitzer and Skinner, 1967; Stevenson, 1976; Blomfield and Sanders, 1977). In the lower B horizon, however, organic complexes should play a minor role. Metal release from this horizon is mainly regulated by the mechanisms of ion exchange or mineral weathering.

7.2. INTERNAL CYCLING

Compared to atmospheric deposition internal cycling proved to be the wholly dominating source of potassium and manganese and the major source of calcium, magnesium and zinc input to the soil surface. These metal ions are readily taken up by the tree roots. A certain amount is accumulated in the biomass and temporarily taken out of the internal cycling. Well above half of the amounts of these metals taken up from the soil were recycled to the soil, either leached from the needles or returned as litterfall. Similar results were obtained by Nihlgård (1970, 1972).

A contrasting element is lead, the internal cycling being small and deposition and mobility of organic matter determining the flux through the ecosystem. The needles absorb lead from the atmosphere effectively: throughfall actually contains

less lead than open-field precipitation. Lindberg and Harriss (1981) also found internal cycling of lead to be negligible and the input to the soil surface of manganese, zinc and cadmium mainly to be part of the internal cycling of these elements.

There are indications that the root uptake of certain metals is increased by accelerated soil acidification. The uptake of rubidium by various organisms is usually greatly favoured by a high soil acidity (Tyler, 1983). In a large number of beech forests in S. Sweden the concentrations of manganese, rubidium and strontium in young buds were positively well correlated to soil acidity (Tyler et al., 1985), and in rhizomes and leaves of *Anemone nemorosa* this was also true of the concentrations of cadmium, manganese, rubidium and zinc (Tyler, 1976b). At an increased availability metals could be expected to accumulate in vital parts of the ecosystem, such as growing organs and the organic top soil (Tyler 1972). Effects on internal cycling may be expected in particular for mobile elements.

7.3. METAL BUDGETS

Run-off data on water flux from the two studied areas and concentrations in lysimeter solutions were used in calculations of the flux of elements through the soil. This introduces certain sources of error. The predictable close relationship between annual gross output of dissolved substances from the soil and total annual run-off (Likens et al., 1977) may, however, justify the use of run-off volume in soil budget calculations. One source of error is that exclusion of viable tree roots from the lysimeter soils caused the soil solution concentrations to deviate to some extent from those in situ. This is particularly true of elements with a high potential of internal cycling, as they would readily be taken up by the tree roots. Examples are potassium and manganese, but also to a certain degree calcium, magnesium and zinc.

An attempt is made to estimate the rate at which the soil store of metals changes. The extractable stores of magnesium, calcium and manganese are lost at a considerable rate from mineral soil and must be effectively resupplied from minerals to keep pace with the leaching; zinc and nickel are lost in minor quantities from the mineral soil. Evidently, there is a potential risk of a shortage to the plants of some elements known to be susceptible to the increases in soil acidity (Bergkvist, 1985) which are nowadays occurring in S. Scandinavia and Central Europe (Butzke, 1981; Falkengren-Grerup, 1985; Hallbäck and Tamm, 1985). There is also a greatly negative budget in soil of the toxic cation aluminium; the budget of cadmium is less negative. The prevailing large leaching in soil of certain metals could reasonably be regarded as a new phenomenon; this was proposed for aluminium in an earlier paper (Nilsson and Bergkvist, 1983).

A net increase in the mineral soil is evident for iron, copper, lead and chromium. In the soil the first sink for these metals is the organic topsoil (litter and mor layer). This soil horizon is often regarded as an almost permanent sink for lead (Benninger et al., 1975; Bowen, 1975; Siccama and Smith, 1978; Smith and Siccama, 1981). In the soils of this study a close relationship was shown between vertical transport of organic matter and lead. Therefore, the uppermost B horizon seems to be the main sink for lead in S. Swedish spruce podzols, though some lead is transported even deeper.

7.4. COMPARISON WITH OTHER STUDIES

Metal budgets have been calculated for the whole microcatchments at Gårdsjön in which the lysimeters of this study are located (Grahn and Rosén, 1983; Hultberg, 1985; Nilsson, 1985b). The general picture from the two different approaches is that the calculated budgets of certain elements are more negative in the lysimeter study, though some elements also have different signs of the balance (Table VII). Sodium, magnesium, calcium, aluminium, chromium and nickel are lost in greater amounts from the soil profile than from the catchment as a whole, where calcium and chromium are almost at balance. Potassium, zinc and cadmium are lost from the soil but have a positive budget in the catchment as a whole. Manganese, copper and lead correspond well in the different studies, the budget of manganese being slightly negative, that of copper and lead positive. Iron is being lost from the catchments as a whole while output from the lysimeter soils is balanced by input to the forest. The differences may partly be attributed to the different methods used: the lysimeters cover only the upper soil horizons of the catchment and the flux is studied at an early stage of transport through the ground. Input to groundwater is not considered in run-off studies, leading to an underestimation of ecosystem losses. Brook water has to a large extent passed through a freely drained soil profile, partly followed by an out-transport through soil layers rich in organic matter. Thus, these two budget approaches are not wholly comparable.

In Denmark, Rasmussen (1985) has used the same lysimeter technique as in this study. Acidity in precipitation is even a little higher at the Danish sites (Freiesleben, 1985). When three planted spruce stands were compared, soil solution concentrations of metals proved to be generally highest in the most acid soil, which was even more acid than the Värnsjö soil. Metal concentrations in soil solution from the lower B horizon in this acid Danish soil were also higher than in the Swedish soils; the concentration of cadmium was four times as high (c. 8-10 mg l⁻¹) as at Värnsjö (c. 2 mg l⁻¹). Tyler (1981) used the same method in a study of the A horizon in a planted spruce forest in S. Sweden. Acid input, soil acidity and soil solution

concentrations of metals were generally the same as at Värnsjö. In these poor, acid soils with a low buffering capacity to acid input, soil acidity must be regarded as the decisive factor in metal release.

In central Europe the problem of metal release and cycling in forest ecosystems has also aroused considerable interest, due to the severe forest decline during the last decade. Metal budgets are available from the heavily polluted Solling mountains (Seekamp, 1977; Heinrichs and Mayer, 1977; 1980). Soil solution concentrations of aluminium were higher in the Swedish soils whereas those of zinc, copper and lead were much higher at Solling. There was a net accumulation in the Solling spruce forest soil of all elements entering the system with atmospheric deposition (except of aluminium and manganese) mainly due to a much higher deposition of most elements than in S. Sweden. The acidity of precipitation is also higher in the Solling area, pH in throughfall being c. 3.4 as yearly mean (Mayer and Ulrich, 1977). Great differences in the mineral soil properties may also be of importance (a residual loess loam at Solling and a sandy-silty glacial till originating from siliceous rocks at the Swedish sites). The mineral soil was also shown to be a source of calcium, magnesium, manganese and aluminium in these studies (Matzner and Ulrich, 1981), as in a *Calluna* heath ecosystem (Matzner and Ulrich, 1980). In a Czechoslovakian spruce forest, in soil solutions from the B horizon even higher aluminium concentrations were found than in this study, c. 20 mg l⁻¹ as annual mean (Lochman, 1983).

Budget studies are also available from a forested watershed in the Black Forest, south FRG (Zöttl et al., 1979; Stahr et al., 1980; Trüby and Zöttl, 1984). The soil parent materials are periglacial solifluction layers and moraines derived from and covering the extremely acid Bärhalde granite. The research area (Bärhalde watershed) is very humid and cool but less polluted than the Solling mountains further north. The ecosystem showed positive budgets of cadmium, copper, nickel, lead and zinc, negative ones of manganese, aluminium, iron, calcium, magnesium, sodium and potassium. Percolating water leaving the subsoil at Bärhalde contains less metals than at Solling (25-50 percent of lead and cadmium; 10 percent of copper), but the deposition input is also lower at Bärhalde. Nevertheless, the differences between the two FRG sites should be partly due to differences in humidity and soil properties. Element release below the rooting zone at Bärhalde is usually comparable to the acid Scandinavian soils for many elements, exceptions being manganese, aluminium and zinc with a higher release rate from mineral soil in the Scandinavian studies.

The element turnover seems also to depend on vegetation type, as was shown in three adjacent stands, a spruce, a beech and a birch stand, having the same parent material (Bergkvist et al. 1985). Throughfall and soil solution were always most acid

in the spruce stand, and concentration and flux of metals usually also highest. The birch soil had the highest pH and lowest concentrations and flow of metals. Aluminium concentration in input to the C horizon was 7, 3 and 1 mg l⁻¹ as yearly mean for the spruce, beech and birch stands, respectively. Nihlgård (1971) showed that plantation of spruce on former beech forest land very rapidly initiated podzolization of the soil. Higher internal production of acids and a more effective trapping of acid aerosols from air in a spruce forest compared to a deciduous forest were regarded as responsible for the differences.

8. Conclusions

It may be concluded that:

1. Lead, copper, iron and aluminium are transported from the A horizon to the B horizon by soluble organic matter. Conditions favouring dissolution of organic compounds also favour this transport.

2. Release of sodium, magnesium, calcium, zinc and cadmium from the A horizon will increase with increasing soil acidity. These elements are released throughout the soil profile and, usually, soil solution concentration continues to increase at least through the B horizon.

3. The precipitation of iron and lead with organic matter in the upper B horizon is almost total. Organic forms of aluminium are also precipitated in the B horizon.

4. An inorganic aluminium species will be released from the mineral soil and increase in concentration through the B horizon.

5. The two forests studied are accumulating iron, copper and lead. At the Värnsjö forest chromium is almost at balance, as is manganese at Gårdsjön.

6. The two forests studied are losing significant quantities of sodium, potassium, magnesium, calcium, aluminium, zinc, cadmium and nickel. The Värnsjö forest is also losing manganese and the Gårdsjön forest chromium.

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LEACHING OF METALS FROM A SPRUCE FOREST SOIL AS INFLUENCED BY EXPERIMENTAL ACIDIFICATION

BO BERGKVIST

Department of Ecology (Plant Ecology), University of Lund, Östra Vallgatan 14, S-223 61 Lund, Sweden.

Abstract. Acidified ($\text{H}_2\text{SO}_4 + \text{HNO}_3$, 3:1) throughfall waters (pH 3.16 and 3.40 as volume weighted means) or control (untreated throughfall water, pH 3.72) were applied for 3.5 yr by an automatic irrigation device to lysimeters containing podzolized spruce forest soils of 0-5, 0-15 and 0-35 cm soil depth. The total volume of the leachates was measured, together with their pH and total content of DOC, Na, K, Ca, Mg, Fe, Mn, Al, Cu, Zn, Cd and Pb and the initial amounts of metals and H in the soil. The main part of H^+ added with the throughfall waters was retained within the soil. Concentrations and fluxes of Mg, Ca, Mn, Zn and Cd in the soil were significantly increased by addition of acidified throughfall waters; K was less affected. As a consequence of lowered flux of DOC in the A horizon as acid input increased, Fe, Al, Cu, and Pb fluxes also decreased. The mobility of these metals in the A horizon was shown to be regulated mainly by the formation of water-soluble organic compounds rather than directly by pH variations. Compared to the control, each yr the additional loss of Mg from the soil profile in the most acid treatment was c. 10% of the currently exchangeable amount.

1. Introduction

The impact of increased atmospheric deposition on forest soils is being paid much attention, especially since damage to forest trees has become a widespread phenomenon. The risk of the pool of necessary nutrients diminishing was pointed out by Mayer and Ulrich (1977) who suspected that the supply of Mg was becoming deficient for the vegetation. Zöttl (1985) considered the deficient nutrient supply as the dominant stress factor causing the forest damage. It has been shown that an improvement of the nutrient supply (especially of Mg) by application of fertilizers can lead to the disappearance of these disease symptoms. In a recent literature review (Nilsson, 1985) it was concluded that a decrease of the pool of exchangeable cations

in podzolized forest soils is probably taking place in S. and SW. Sweden. Root damage due to high concentrations of toxic metals is also likely to develop. It has been stated that a successive decrease of exchangeable Ca and a concomitant increase of available Al can cause damage to tree roots (Ulrich et al., 1979; Ulrich, 1983).

This study is part of a larger project, on deposition and cycling of metals in forest ecosystems financed by the Swedish Environmental Protection Board. The objectives of the study are to evaluate the extent to which an accelerated but moderate acidification of a podzolized forest soil can cause high concentrations of metals in soil solutions; to quantify metal losses from the soil; and to relate these losses to the soil pool.

2. Materials and Methods

A mature mixed-coniferous forest situated in southwest Sweden was chosen for the experiment. The main tree species is Norway spruce (*Picea abies*); some Scots pine (*Pinus silvestris*) also occurs, but does not influence the studied soil plots. The study area (Värsjö) is situated about 130 km NNE of Lund. The stand is mainly even-aged, the spruce being c. 80 yr. A few species dominate the vegetation of the forest floor: the grass *Deschampsia flexuosa*, the dwarf-shrub *Vaccinium myrtillus*, the mosses *Ptilium crista-castrensis* and *Pleurozium schreberi*. Areas devoid of vegetation are found beneath the tree crowns. No shrub layer is usually present. The topography is characterized by low hills of sandy-silty glacial till, originating from siliceous rocks, poor in carbonates, surrounded by mires. The soil is generally very deep and freely drained. It may be characterized as an Fe podzol, with a 7-10 cm purely organic litter+mor horizon ($A_{00}+A_0$), a 5-12 cm greyish mineral horizon (A_2), and a 25-35 cm illuvial horizon (B_1). The vertical distribution of organic matter, clay content, pH and metal content in the soil profile is shown in Tables I and II.

The mean monthly temperature of the warmest month is c. 16 °C, of the coldest month c. -2 °C. 1980 and 1981 were colder than normal; 1982, 1983 and 1984 were warmer than normal. Mean annual precipitation is c. 785 mm according to data from four meteorological stations within 15 km (Elleson, 1985). The main part of the precipitation falls in late autumn and winter. Snow cover is seldom stable throughout the winter. However, the two winters 1980/1981 and 1981/1982 were characterized by a considerable snow cover (20-50 cm) of above-normal duration.

TABLE I

Content of organic matter as organic C and clay (percent of the dry weight) and pH-H₂O and pH-KCl in the studied soil.

Soil horizon	Soil depth, cm	Organic matter	Clay	pH H ₂ O	pH KCl
A ₀₀ +A ₀	0-5	48	1.1	3.64	2.81
A ₁ +A ₂	5-15	9	1.6	3.76	2.99
B ₁	15-35	2.9	1.0	4.19	4.00

TABLE II

Content of metals and H in the studied soil (g m⁻²)

Acid digestible ("total")*					Extractable**			
	0-5	5-15	15-35	Σ0-35	0-5	5-15	15-35	Σ0-35
Na	5.1	34	60	99	0.96	2.3	1.9	5.2
K	4.8	36	106	147	7.5	3.8	4.7	16
Mg	11	70	232	313	3.7	2.9	1.4	8
Ca	53	242	674	969	9.7	18	4.8	33
Al	44	492	3040	3580	0.24	9	96	105
Fe	74	1260	5010	6340	0.15	2.9	12	15
Mn	5.9	28	87	121	0.28	1.7	0.7	2.7
Cu	0.2	0.2	0.6	1.1	0.04	0.03	0.04	0.11
Zn	1.1	2.5	6.7	10.3	0.83	1.4	1.3	3.5
Cd	-	-	-	-	0.007	0.009	0.009	0.03
Pb	2.3	2.1	2.9	7.2	1.7	1.7	1.3	4.7
H	-	-	-	-	0.30	1.04	1.3	2.6

* Conc. HNO₃:HClO₄ (4:1)

** Na-EDTA: Cu, Zn, Cd, Pb

Acid NH₄Ac (pH 4.8): Na, K, Mg, Ca, Al, Fe, Mn

KCl: H

The lysimeters were constructed in plexiglass. Soil cores were taken close together beneath the spruce crowns. They were lacking any vascular vegetation. The cores were taken with steel cylinders and transferred to the lysimeters with a minimum of disturbance. Then the lysimeters were installed in the soil at the original positions. They were equipped with irrigation devices and Erlenmeyer flasks (Duran glass) for the collection of soil water. For a more detailed description of lysimeter design and installation see Tyler (1981) or Nilsson and Bergkvist (1983).

Three different soil depths were chosen for each set of lysimeters. They represented approximately the A₀₀ + A₀ horizons (depth 0-5 cm), the A horizon

including most of A₂ (depth 0-15 cm), and the A horizon + the B₁ horizon (depth 0-35 cm).

The diameters of the lysimeters were 290 mm (0-5 and 0-15 cm) and 190 mm (0-35 cm). Three different sets of lysimeters were installed which makes one lysimeter for each treatment at a given soil depth. Throughfall water was collected in 15 systematically distributed plastic funnels (diam. 30 cm) connected to plastic bottles. Plastic nets in the bottom of these funnels trapped the litter fall which was also collected. During winter an equal number of plastic buckets was used (diam. 30 cm). Polyethylene was used in all plastic equipment.

The throughfall waters were filtered (filter papers Munktell OOK), mixed in a large plastic barrel and divided into three identical aliquots. One aliquot was acidified by H₂SO₄ and HNO₃ (3:1) to pH 3.30, the second one to pH 3.00 and the third one was left untreated as a control. The waters were then placed in the irrigation device and automatic irrigation of the lysimeters continued during 5 weeks after each refill. In each irrigation device the water was put into a 5-litre plastic bottle and flowed through a solenoid valve to an irrigation vessel of plexiglass placed 10 cm above the lysimeter as a shelter against natural rain. The perforated (Ø 1.5 mm perforation, 2.5 cm distance) bottom was covered by a filter paper (Munktell OOH). The battery-operated solenoid valve opened two times a week and each time c. 6 mm water was added to the soil.

The irrigation device was only operating from March/April to November/December. One set of lysimeters (0-5, 0-15 and 0-35 cm) received the pH 3.00 throughfall, a second set the pH 3.30 and a third set received the untreated throughfall. During the winter they received snow and rain in ambient amounts and properties. Appropriate amounts of litterfall were given to the lysimeter soils at each sampling time during the sheltered period.

The lysimeters were installed in August 1980. The experiment started on October 1, 1980 and ceased on April 7, 1984. The collection interval was about 5 weeks.

Total concentrations of 11 metals in the drainage waters from the lysimeters were measured by AAS technique: Na, K, Ca, Mg, Fe, Mn, Al, Cu, Zn, Pb and Cd. Furthermore, pH and dissolved organic C (DOC) were determined, DOC by infrared technique using a Beckman 915B carbon analyser. Soil parameters (organic matter, clay content, pH and content of metals) are from a budget study in the immediate vicinity (Bergkvist, 1986). Detailed descriptions of field sampling, sample pretreatment and analysis are found in Tyler (1981) and Nilsson and Bergkvist (1983).

3. Results and Discussion

3.1. GENARAL CONSIDERATIONS AND HYDROGEN FLUX INTO AND OUT OF THE SOIL

Data are presented in the following ways: (1) Mean concentrations of metals and DOC for the whole period, 3.5 yr; (2) Extractable and "total" amounts of metals in the soils; (3) Calculations of metal budgets of the soils; (4) Stepwise regression (multiple) analysis of variable interrelation.

Concentrations are calculated as mg l^{-1} for DOC, Na, K, Ca, Mg, Fe, Mn and Al; as $\mu\text{g l}^{-1}$ for Cu, Zn, Pb and Cd. Stores of metals in soils are calculated as g m^{-2} ; the flow of metals as $\text{g m}^{-2} \text{yr}^{-1}$.

The average annual precipitation during the experiment was 950 mm. Throughfall is c. 60% of the precipitation, more during years with above normal precipitation sums. As the lysimeters were irrigated by throughfall water collected in the study area, the actual amounts of precipitation water were governing the amount added to the lysimeters. The yearly mean sum of throughfall added to the lysimeters (including ambient throughfall during winter months) was 620 mm or 65% of the precipitation. As the lysimeters received artificially acidified water only during the irrigation period, c. 8 mo yr^{-1} , the resulting weighted mean pH for the whole volume added during three years was 3.16 for the 3.00 treatment and 3.40 for the 3.30 treatment. The pH of the total volume added to the control lysimeters was 3.72. The different treatments are in the following text called "pH 3.16", "pH 3.40" and "control" (= pH 3.72). In each step the added amounts of H ions were approximately doubled (Table III).

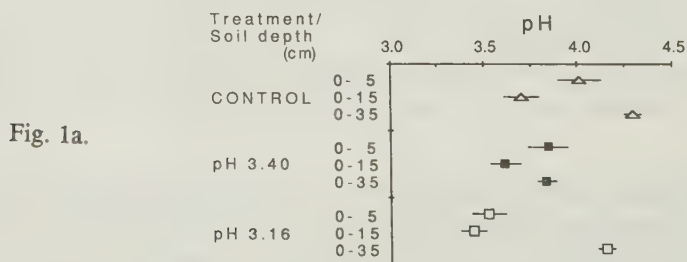


Fig. 1. Mean concentrations, and the 95% confidence interval, in the leachates from the three lysimeter sets (see text) irrigated with throughfall waters of different acidity. $n=33$. (a) pH; (b) DOC, Na, K, Ca, Mg, Fe, Mn and Al as mg l^{-1} ; Cu, Zn, Cd and Pb as $\mu\text{g l}^{-1}$.

In a spruce stand in S Sweden, due to the acid deposition in the region, the throughfall pH varies between 3.20 and 4.20 during the year, with extremes of 3.00.

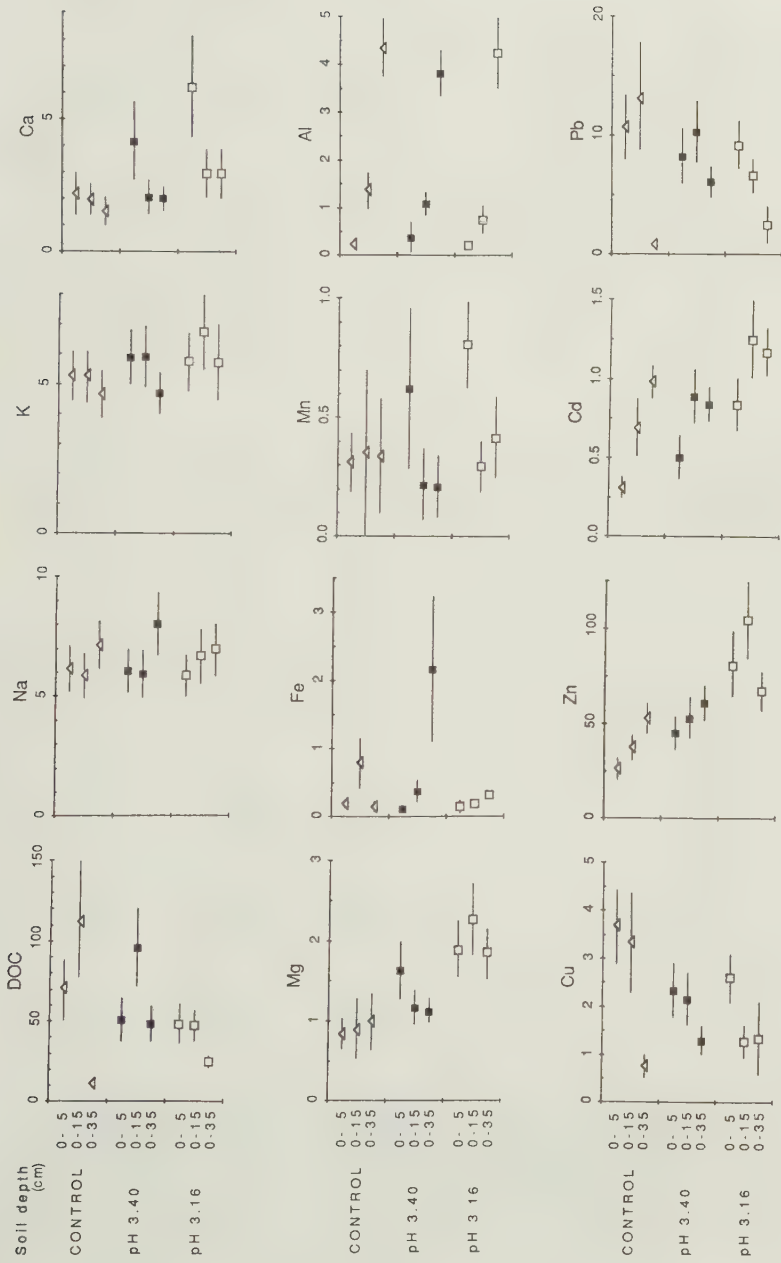


Fig. 1b.

TABLE III

Total cumulated fluxes of metals, H and DOC during three years of the experiment ($\text{g m}^{-2} \text{ 3 yr}^{-1}$).

Treatment	H	DOC	Na	K	Mg	Ca	Fe	Mn	Al	Cu	Zn	Cd	Pb
Soil depth cm													
Input to soil:													
Control	0.36	-	10.4	7.2	3.3	6.4	0.24	1.6	0.39	0.007	0.12	0.0008	0.024
pH 3.40	0.73												
pH 3.16	1.3												
Output from soil:													
Control													
0-5	0.21	122	10.2	8.5	1.3	3.1	0.35	0.43	0.41	0.006	0.04	0.0005	0.019
0-15	0.41	195	9.5	9.1	1.3	2.7	1.5	0.39	2.4	0.006	0.06	0.0012	0.023
0-35	0.10	20	14.1	9.5	1.7	2.5	0.24	0.67	8.6	0.001	0.10	0.0019	0.002
pH 3.40													
0-5	0.28	86	9.8	9.1	2.6	5.6	0.24	0.93	0.59	0.004	0.07	0.0008	0.015
0-15	0.46	167	9.5	10.0	1.9	2.9	0.73	0.21	2.0	0.004	0.08	0.0015	0.017
0-35	0.32	110	16.3	10.4	2.4	4.0	0.47	0.43	8.1	0.002	0.13	0.0018	0.013
pH 3.16													
0-5	0.57	81	9.5	8.8	3.1	9.5	0.29	1.3	0.37	0.004	0.13	0.0014	0.016
0-15	0.67	84	11.5	12.0	3.9	4.5	0.37	0.40	1.43	0.002	0.17	0.0022	0.012
0-35	0.19	60	15.6	12.5	4.4	5.8	0.73	0.92	10.6	0.003	0.16	0.0028	0.004

The mean pH of the control (3.72) is a normal yearly mean value. Stemflow is mostly below 3.20 (Bergkvist, 1986; Bergkvist et al., 1986). The experimental treatments must therefore be considered realistic, avoiding shock effects on the biological systems in the soil.

Acid supplied with the leaching solutions was partly neutralized by the soil, though acidity in soil leachates was markedly increased when acidity of throughfall inputs increased (Table III). The outflow from the uppermost topsoil (0-5 cm) is less than half of the inflow; after passage of the B horizon (0-35 cm) most of the acidity added was retained within the soil. A t-test of the means of the 3.5 yr in Figure 1a shows that the lowering of pH in soil leachates from the A horizon is highly significant when the most acid treatment is tested against the other acid treatment and against the control (Table IV).

TABLE IV

Test of the differences between the means in Figure 1 (t-test, $p < 0.001$). a = between the control and the pH 3.40 treatment, b = between the control and the pH 3.16 treatment, c = between the two acidification treatments. "+" means a significant increase and "-" a decrease. n = 33.

	0-5	0-15	0-35
Na			
K			
Ca	+b		+b
Mg	+a +b	+b +c	+b +c
Fe		-c	+a +b -c
Mn	+c		
Al			
Cu	-a	-b -c	
Zn	+a +b +c	+b +c	
Cd	+b +c	+b	
Pb		-b	+a -c
DOC		-b -c	+a +b -c
pH	-b -c	-b -c	-a -b +c

Unexpected fluctuations of the depth of the transition zone between the A₂ and B₁ horizons produced differences in that part of the B₁ horizon which was included in each 0-35 cm lysimeter. In a podzol, dissolved organic matter precipitates in the upper part of the B horizon (see e.g. Petersen, 1976) and only minor quantities pass through the deeper B horizon. An expected concentration of DOC in soil leachates was found in the control at this soil depth, but not in the two acid treated lysimeters. In both of these, most probably due to fluctuations of the depth of the transition zone,

DOC concentrations were higher than in the control. In particular, the pH 3.40 treated lysimeter deviates. All comparisons of the 0-35 lysimeters must therefore be made with caution.

Due to the use of lysimeter technique (root uptake by the trees was excluded) concentrations and flow of certain elements and water in soil leachates from the lysimeter soils may be over-estimations of the actual situation in situ.

3.2. LEACHABILITY OF METALS

The leachability as affected by an increase in acidity of the leaching solutions differs greatly among metals. It is evident from Figure 1b and Tables III and IV that Ca, Mg, Zn and Cd throughout the soil profile and Mn in the mor layer (0-5 cm) have higher concentrations in soil leachates and greater outflow from soil when more acid is added to the soil. This is in accordance with the findings of Tyler (1978), in a laboratory study of the leaching of heavy metals from metal-polluted and unpolluted mor layers. No significant increase in soil leachate concentrations was found for Na, indicating that weathering rate was not increased as the acid input increased. Nor was K concentrations significantly increased, though the trend for K is toward higher output from soil as leaching solutions become more acid.

The influence of acid precipitation on the leaching of K, Ca and Mg has attracted special interest in the discussion of acid rain impact on terrestrial ecosystems. It has been shown experimentally that an increased acidity of artificial rain most significantly increases the Ca and Mg loss from soil; K appears to be less sensitive (Abrahamsen et al., 1977; Tamm et al., 1977; Abrahamsen, 1980; Abrahamsen and Stuanes, 1980; Bjor and Teigen, 1980; Cronan, 1980; Farrell et al., 1980; Stuanes, 1980; Morrison, 1983). In an experimentally acidified mountain stream in the Hubbard Brook Experimental Forest, USA, (mean pH 4.0) streamwater concentrations of Al, Ca, Mg, K, Mn, Fe and Cd increased with acidity (Hall and Likens, 1980). In a study where lysimeter soils were irrigated with waters of different acidity, only in the most acid treatment was an effect on soil chemistry shown. A decrease in extractable amounts of Ca and Mg, decreased base saturation and soil pH were limited to the uppermost 15 cm. At 15-30 cm depth extractable amounts of Ca and Mg were increased compared to control, indicating transport of these cations from the soil surface (Lee, 1985).

The influence of acidification on soil budgets of trace elements has not attracted as much concern as the macronutrients but some studies are reported. The mobility of Cd and Zn was shown to increase with soil acidity (Esser and EL Bassam, 1981; Brümmer and Herms, 1983; Scokart et al., 1983) and the same was also shown for Mn (Bjor and Teigen, 1980; Norton et al., 1980).

In the present study, the release of Al, Fe, Cu and Pb did not seem to be enhanced at all by the acidity added to the soil. The release in the A horizon was in fact lowered by the addition of more acid to the soil. The release of these metals was closely related to the release of organic matter. The DOC content of soil leachates was significantly lowered in the A horizon when acid was added to the soil and so were the concentrations of Fe, Cu and Pb in the most acid treatment. Strong acidification seems to reduce the litter decomposition rate. It was demonstrated in an early study that the decomposition of humus and cellulose declined in direct proportion to the pH decrease caused by the addition of elemental sulphur to a mineral soil (White et al., 1934). Later studies have verified these findings. Tamm et al. (1977) obtained data suggesting that the addition of H_2SO_4 to soil reduced the C mineralization rate in humus. Irrigation with pH 2 water reduced birch litter decomposition, while pH 3 did not (Hågvær and Kjendal, 1981). In an acid "rain" experiment with a pine forest soil (Bååth et al., 1979), pH 2.0 water caused a reduction in soil respiration but with pH 3.0 no statistically significant effect was noted.

The high correlation of Fe, Cu, Pb and Al with DOC in the A horizon disappears in the B₁ horizon. At least for Al this is in accordance with a speciation study of Al reported by Nilsson and Bergkvist (1983), where organic and inorganic Al species in soil leachates from different soil horizons in a podzol were determined. Almost all Al in the A horizon soil leachates was organically bound, compared to only c. 20% in the lower B horizon. According to these findings no pH-sensitivity of Al is to be expected in the A horizon. No sensitivity of Al in the mineral part of the soil was detected. This lack of pH-sensitivity of Al was also found by Cronan (1980). But in other acidification experiments an increase of Al concentrations with acidity was found (Abrahamsen and Stuanes, 1980; Bjør and Teigen, 1980; Norton et al., 1980). The Al release from the mineral soil seems to be a very fast process below a critical pH value. If the Al concentrations of the soil solutions from the deeper B horizons of a spruce forest soil are plotted against the solution pH, the curve bends very sharply upward at a pH below 4.4 (Tyler et al., 1985). A pH decrease of 0.2 units from pH 4.4 results in an increase of the Al concentration from 2 to 10 mg l⁻¹. In the upper part of the soil the upward bend of the curve starts at a lower pH, indicating a gradual diminution of the exchangeable and easily weatherable pools in the soil. In this study only the upper B horizon is included in the lysimeters. The added amounts of acid during the experiment were not sufficient to increase the Al mobility. A dramatic increase in Al concentrations was demonstrated by Teigen et al. (1976) and Abrahamsen (1983) when "rain" acidity increased from pH 3.0 to pH 2.0; Al concentration in the effluent increased from an average of 3 to 48 mg l⁻¹.

Tyler (1978) showed in the above mentioned laboratory experiment with mor layers that Cu and Pb were also released when enough acid had been added to the

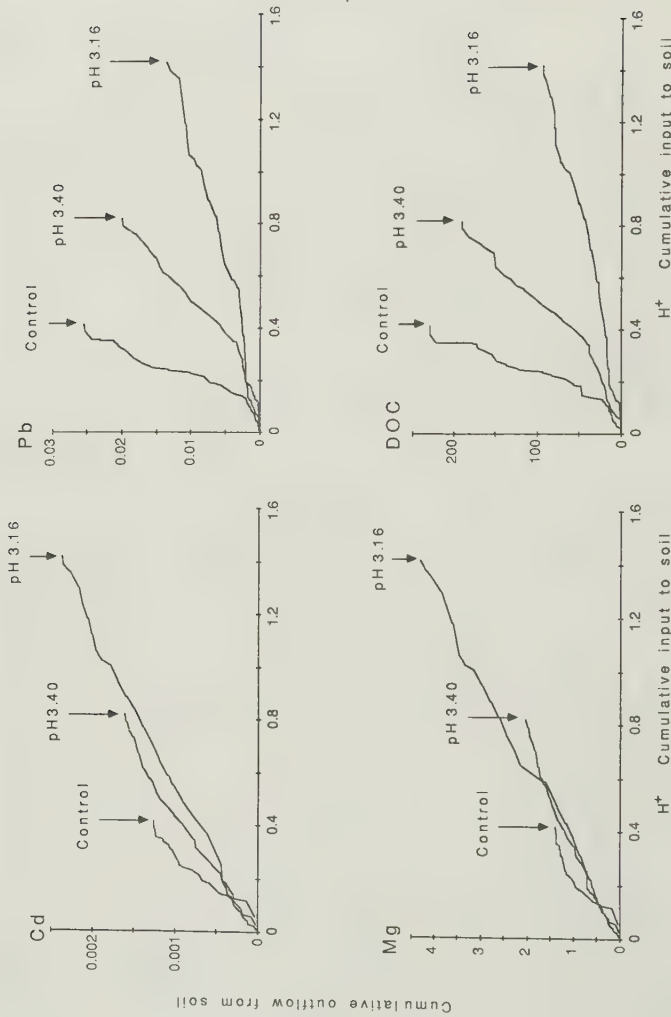


Fig. 2. Cumulative sum in outflow (gross, Y-axis) of Mg, Cd, Pb and DOC in the leachates from the three 0-15 cm lysimeters from each of the different acid treated lysimeter sets, during the whole experiment (3.5 yr) and on the X-axis, cumulative sum of H^+ added to the lysimeter soils by irrigation with throughfall waters and in ambient amounts during the winters ($g\ m^{-2}$). The arrows indicate the amounts of H^+ added during 3.5 yr by each treatment.

soil. In fact, a weak tendency toward increased Cu output from the B₁ horizon is indicated in the strongest acid treatment in the present study (Table III and Fig. 1b).

Great differences between the leachability of Mg and Cd on the one hand and Pb on the other and the role of humus are evident from Figure. 2. The cumulative sums, during 3.5 yr, of metals and DOC in gross outflow from the A horizons (0-15 cm) at the different acid treatments and the control are plotted against the cumulative sums of H added to the soils during the same period. Mg and Cd are released from the A horizon almost proportionately to the input of acid. The amount of Mg outflow during 3.5 yr in the pH 3.16 treatment corresponds to a 10-yr outflow from the control soil. In Cd the corresponding time is 7 yr. Interestingly, the outflow of Pb was lowered in the acid treatments. The Pb graph (Figure. 2) is almost a reflection of the DOC graph (Figure. 2) and the release of organic compounds governs the Pb release entirely. These close relationships between Pb and humus release and between the acidity of the soil system and release of Mg and Cd were also shown by Tyler (1981) at ambient soil pH variations.

3.3. STEPWISE REGRESSION ANALYSIS

As an attempt to find the variables regulating the mobility of the metals studied, simple correlation, partial correlation, and stepwise regression analysis were performed on the material of the pH 3.16 treatment (Table V). pH in added throughfall water, and pH, DOC content, Σ base cations (Na, K, Ca and Mg) and Mn concentrations of soil solutions have been treated as independent variables with respect to other metals (inorganic anions (eg. sulphate, nitrate and chloride) were not measured, though they probable to a certain extent influence the transport of metals in soils). The analysis shows for each metal the share of dependent variability which might be explained by the variability of one, two or several of the independent variables. Only if the variability accounted for was greater than c. 60 % is the metal included in Table V.

Zinc shows a close inverse relation to pH, and a positive correlation to Mn both in the mor layer and in the entire A horizon. Σ base cations also shows a close positive relation to Zn. With the included variables, 87 and 72%, respectively, of the variability is accounted for in the two horizons.

TABLE V

Multiple relations between metal concentrations of lysimeter solutions and certain variables, according to stepwise regression analysis of the pH 3.16 treatment. Independent variables: pH in throughfall, pH, DOC content, Σ base cations (Na^+ , K^+ , Ca^{2+} , Mg^{2+}), and Mn concentrations of soil (lysimeter) solutions. a after value of simple and partial r indicates a highly significant ($p < 0.01$) correlation, 100 r^2 the percentage variability accounted for by the variables entered. $n = 33$.

Step no., variables entered	mul- tiple 100 r^2	simple r	par- tial r	Step no., variables entered	mul- tiple 100 r^2	simple r	par- tial r
Zn (0-5 cm) (87)				Zn (0-15) (72)			
1. pH soil sol.	72	-0.85a	-0.44	1. pH soil sol.	51	-0.72a	-0.65a
2. Mn	83	0.81a	0.61a	2. Mn	68	0.21	0.44
3. DOC	86	0.07	-0.45a	3. Σ base cations	72	0.65a	0.30
4. Σ base cations	87	0.79a	0.23	4. DOC	72	0.30	-0.12
5. pH throughfall	87	-0.77a	-0.22	5. pH throughfall	72	-0.61a	-0.04
Cd (0-5 cm) (75)				Cd (0-15) (80)			
1. pH soil sol.	66	-0.81a	-0.28	1. pH soil sol.	72	-0.85a	-0.76a
2. Σ base cations	72	0.77a	0.29	2. Σ base cations	79	-0.61a	0.51a
3. pH throughfall	74	-0.79a	-0.28	3. DOC	79	0.29	-0.18
4. Mn	75	0.68a	0.18	4. pH throughfall	80	-0.65a	0.18
Cd (0-35 cm) (55)				Cu (0-35 cm) (63)			
1. pH throughfall	31	-0.56a	-0.25	1. Mn	47	0.69a	0.76a
2. DOC	42	-0.50a	-0.52a	2. pH soil sol.	59	0.05	0.49a
3. Σ base cations	48	0.43	0.38	3. pH throughfall	63	0.33	0.28
4. pH soil sol.	54	0.17	0.28				
Mg (0-5 cm) (77)				K (0-15 cm) (60)			
1. pH soil sol.	69	-0.83a	-0.38	1. pH throughfall	46	-0.67a	-0.58a
2. Mn	74	0.71a	0.29	2. Σ base cations	51	0.56a	0.30
3. pH throughfall	76	-0.78a	-0.22	3. pH soil sol.	58	-0.32	0.37
4. Σ base cations	77	0.71a	0.19	4. DOC	60	0.48a	0.23

In the mor layer and in the entire A horizon, pH shows a close inverse relation to Cd concentration and accounts for 66 and 72% of the Cd variability, respectively. Σ base cations increases the variability accounted for to 77 and 79%, respectively. At the level of the upper B horizon, pH of the added throughfall water accounts for only 31% though if the other variables are also included 54% of the Cd variability is accounted for.

Manganese is the variable first entered when Cu is the dependent variable, and accounts for 47% of the Cu variability in the soil profile down to the upper B horizon.

The pH of the system shows a close inverse relation to Mg concentrations and accounts for 69% of the variability of Mg in the mor layer.

pH of the added throughfall shows a close inverse relation to the variability of K. If Σ base cations and pH in soil solution are also included 58% of the variability is accounted for.

In the pH 3.16 treated soils the acidity of the system seems to be very important for the mobility of these metals. Interestingly, Mn appears to be very important for the mobility of Zn, Cu and Mg. It is known (Taylor and McKenzie, 1966; Sidhu et al., 1976) that manganiferous nodules in soils contain varying amounts of other metals, eg. Zn, Cu and Mg. Factors affecting the solubility of these concretions also affect the mobility of the associated metals.

4. Conclusions

It seems reasonable to conclude that increased soil acidification by acid rain may increase the concentrations of several metals in the soil solution, eg. Ca, Mg, Mn, Zn, Cd and (as was shown elsewhere) eventually also Al. Because of increased losses from soil of nutrients, and because there are indications that soil weathering rate does not keep pace with losses, there is a potential risk that exchangeable stores will decrease, with consequences for plant uptake. Compared to the control, each yr the additional loss of Mg in the most acid treatment was c. 10% of the currently exchangeable amount in the soil. Biological recycling of nutrients by decomposition and uptake may be impeded. The concentrations of eg. Cd and (as was shown elsewhere) Al are increased to such an extent that risks of root injury cannot be disregarded.

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LEACHING OF METALS FROM FOREST SOILS AS INFLUENCED BY TREE SPECIES AND MANAGEMENT

BO BERGKVIST

Department of Ecology (Plant Ecology), University of Lund, Östra Vallgatan 14, S-223 61 Lund, Sweden.

Abstract. The leaching of metals (Na, K, Mg, Ca, Fe, Mn, Al, Cu, Zn, Cd, Pb, Cr and Ni) in a brown forest soil (Sjöbo) and a podzol (Horröd) with adjacent stands of spruce, beech and an open regeneration area in S Sweden were quantified using lysimeter technique. The two localities differed in soil properties: glacialfluvial sand deposit at Sjöbo; acid glacial till, poor in carbonates, at Horröd. Generally, the leaching of base cations was greatest from the brown forest soil, while the leaching of Al was greater from the podzol. Soil solution pH was lowest in the spruce forests, highest in the regeneration areas. The spruce increased soil acidification and leachability of metals most pronouncedly in the podzol. Soil acidification and leaching of metals were usually less under beech than under spruce. Soil solution metal concentrations were generally lowest in the regeneration areas, as was the outflow of metals. In an opening outside the spruce canopy at Horröd soil acidification did not penetrate as deep as beneath the canopy; also the metal flux was considerably lower in the opening. In the spruce soil at Sjöbo and in all soils at Horröd Al was the metal most clearly affected by variations in soil acidity. The solubility of Al increased suddenly within a small pH range (4.5-4.0) in the B horizon. Concentration of Al in soil solution increased from 2 to 10 mg l⁻¹ when pH decreased from 4.4 to 4.2. In the brown forest soil at Sjöbo, particularly in the beech stand and in the regeneration area, the increase of base cation concentrations corresponded to the soil acidity in this pH range.

1. Introduction

Acid deposition has probably increased the rate of base cation leaching in most soils which are exposed to it, and there are indications of diminishing nutrient pools from different parts of the northern hemisphere (Norton et al., 1980; Raish, 1983; Nilsson, 1985). Soil properties and chemical state are important factors regulating

the effect of acid deposition. In southern Sweden, atmospherically derived sulphuric and nitric acid has led to increased Al concentrations in soil solution in very acid forest soils (Nilsson and Bergkvist, 1983). Also other metals have elevated solution concentrations in those soils, eg. Cd (Bergkvist, 1986) as in very acid Danish soils (Rasmussen, 1985). In soils within the cation exchange buffer range ($\text{pH} \geq 4.2$) increased soil acidity leads to the liberation and leaching of Ca and Mg, while the leaching of Al is the buffer reaction in soils within the aluminium buffer range (pH 4.2 to 2.8) (Ulrich, 1983).

Recent comparisons where old soil investigations were repeated have shown a considerable decrease in soil pH in all forest soils investigated in central and northern Europe during recent decades (Butzke, 1981; Falkengren-Grerup, 1985; Hallbäck and Tamm, 1985). The degree to which the acid deposition has increased the soil acidity varies according to e.g. soil base cation reserves, weathering rate and the amount and duration of acid deposition impact.

The influence which different tree species exert on soil acidification, nutrient cycling and soil properties is often a subject of debate. Even if a considerable soil acidification has occurred in all forest types investigated, the dominating tree species is quite important for the metal cycling and acid-base properties of the soils. The acidifying potential of the spruce is definitely greater than that of deciduous trees, e.g. beech or birch. There are many reasons for this. Dry deposition is greater to a spruce stand, due to a larger aerosol trapping leaf area, particularly in winter (Höfken and Gravenhorst, 1982; Mayer and Ulrich, 1982). The spruce canopy increases the acidity of incident precipitation considerably, metals and sulphur being enriched, and the pH is usually greatly decreased by passage of the spruce canopy, at least in rural areas. Incident precipitation water passing through a beech canopy becomes less enriched in or even loses metals (Nihlgård, 1970; Heinrichs and Mayer, 1980; Mayer, 1981; Bergkvist et al., 1986); the internal production of acids is also greatest in a spruce stand (Matzner and Ulrich, 1981). When old farmland or beech-forest soil was planted with spruce, the soil deteriorated rapidly (Nihlgård, 1971; Bråkenhielm, 1977).

In the present investigation, a brown forest soil and a podzol, each with adjoining stands of Norway spruce (*Picea abies*), European beech (*Fagus sylvatica*) and open regeneration areas from spruce are studied. In these two different soil types the aim is to quantify the influence of tree species and land management on soil acidification processes and on the leachability and annual flow of metals between different soil horizons.

2. Site Description

The investigation was carried out in two different forest areas in south Sweden. The southern study area (Sjöbo) is situated c. 45 km ESE Lund, south Sweden. It is developed on a major glacifluvial sand-deposit. The soil is very deep and freely drained. In all stands the soil is an acid brown forest soil with mull (Fig. 1). The aggregation is weak in the mull horizon (A₁) in the beech forest, and a 2-4 cm litter layer is visible throughout the year. In the spruce forest the A₁ horizon is in an intermediate state between mull and mor, somewhat compacted, with bleached mineral grains (not visible in the beech mull), particularly at the bottom of the horizon. Also in the mull horizon of the regeneration area, bleached mineral grains are visible. As in the spruce stand there are traces of a thin bleached A₂ horizon. The brown earth horizon (B) is without notable illuviation in all stands, and generally the humus content decreases downwards. The features of the soils are shown in Fig. 1 and Table I, the vertical distribution of organic matter, clay content and pH in Table II and the distribution of metals in Fig. 2.

The spruce stand at Sjöbo is an even-aged, first forest generation on former open land, planted c. 50 yr ago (Table I). The vegetation of the forest floor is dominated by the grass *Deschampsia flexuosa* and the herb *Oxalis acetosella*. Also the beech stand is mainly even-aged, the beech being c. 100 yr. The vegetation of the forest floor is characteristic of medium rich beech forests in the region. The regeneration area was windthrown (and cleared from trees, spruce) in 1967, eleven years before this study started; therefore the peak concentrations of nutrients in run-off after clear cut (cf. Bormann and Likens, 1981) had passed. The area was planted with small spruce plants (c. 0.5 m height), but they did not influence the plots studied. The vegetation is dominated by grasses; the shrub *Rubus idaeus* also thrives well.

The northern study area (Horröd) is situated c. 70 km NNE Lund. The structure of the stands is shown in Table I. A characteristic feature of the landscape is low hills of sandy- silty glacial till, originating from siliceous rocks, poor in carbonates, partly surrounded by mires. The stands are developed on one of these low hills. The soil is generally very deep and freely drained with a low water-table, except on occasions with excess water input (e.g., at snowmelt or heavy winter rain). The soil is podzolized, being an iron podzol, especially characteristic in the regeneration area. In the beech and the spruce forests the precipitation of humus in the upper B horizon is more pronounced, making that horizon slightly brown colored. The features of different soil horizons are shown in Fig. 1 and Table I,

TABLE I

Vegetation, soil and equipment at the studied sites.

Site/Vegetation Soil	Spruce	Spruce (opening)	Beech	Regener. area
HORRÖD:				
Tree layer:				(cleared 1970)
age (yr):	60	-	90	-
diam (cm):	25-30	-	30-40	-
canopy cover %	40-50	-	60-70	-
Field and bottom layer species	<i>D.flexuosa</i> <i>O.acetosella</i> <i>P.schreberi</i> <i>Dicranum spp.</i>	<i>D.flexuosa</i> <i>O.acetosella</i> <i>Polytrichum</i> <i>formosum</i>	<i>D.flexuosa</i> <i>Majanthe-</i> <i>mum bifo-</i> <i>lium</i>	<i>D.flexuosa</i> <i>Pot.erecta</i> <i>Festuca</i> <i>ovina</i>
Soil*:	p	p	p	p
C a (15-35 cm)†	4.4	4.1	4.3	6.1
Al (15-35 cm)†	79	44	93	111
Lysimeter**	0-5	0-5	0-5	0-5
installations (cm):	0-15 0-35 0-55	0-15 0-35 0-55	0-15 0-35 -	0-15 0-35 -
SJÖBO:				
Tree layer:				(cleared 1967)
age (yr):	50		100	-
diam (cm):	30		45	-
canopy cover %	40-50		70-80	-
Field and bottom layer species	<i>D.flexuosa</i> <i>O.acetosella</i> <i>Rubus</i> <i>ideaus</i>		<i>Milium</i> <i>effusum</i> <i>Poa nem.</i> <i>G.odoratum</i> <i>A.nemorosa</i>	<i>D.flexuosa</i> <i>Agrostis</i> <i>tenuis</i> <i>Rubus</i> <i>ideaus</i>
Soil:	b		b	b
C a (15-35 cm)†	4.0		10	14
Al (15-35 cm)†	66		80	81
Lysimeter**	0-5		0-5	0-5
installations (cm):	0-15 0-35 0-55		0-15 0-35 0-55	0-15 0-35 -

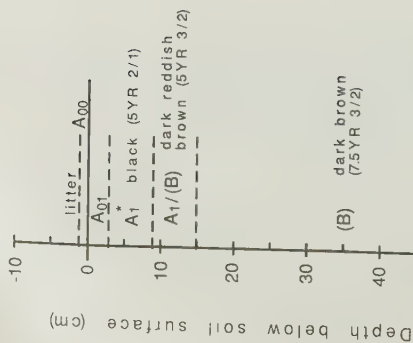
p=podzol, b=brown forest soil.

* Mineral soil parent material: at Horröd sandy-silty glacial till originating from siliceous rocks; at Sjöbo glaciifluvial sand-deposits.

** 0-5, 0-15, 0-35 installed Sept 1978; 0-55 Sept 1979.

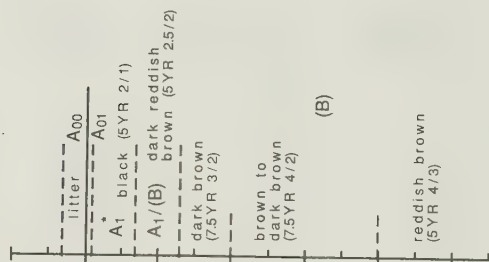
† Extractable by NH₄Ac (pH 4.8), g m⁻².

Spruce

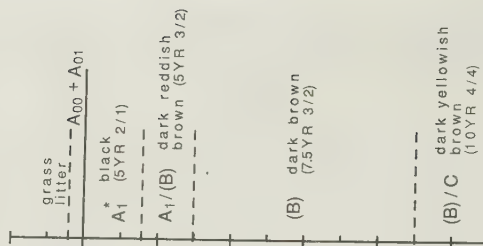


* intermediate between mull and mor
with bleached minerals
(a weak tendency to A₂)

Beech



* mull (weak
aggregation)

Regeneration
area

* mull with bleached minerals
(a weak tendency to A₂)

Fig. 1a. Sjöbo

Fig. 1. Profile descriptions of the studied soils. Colour names and codes (for moist soils) are according to Munsell (1973).

HORRÖD

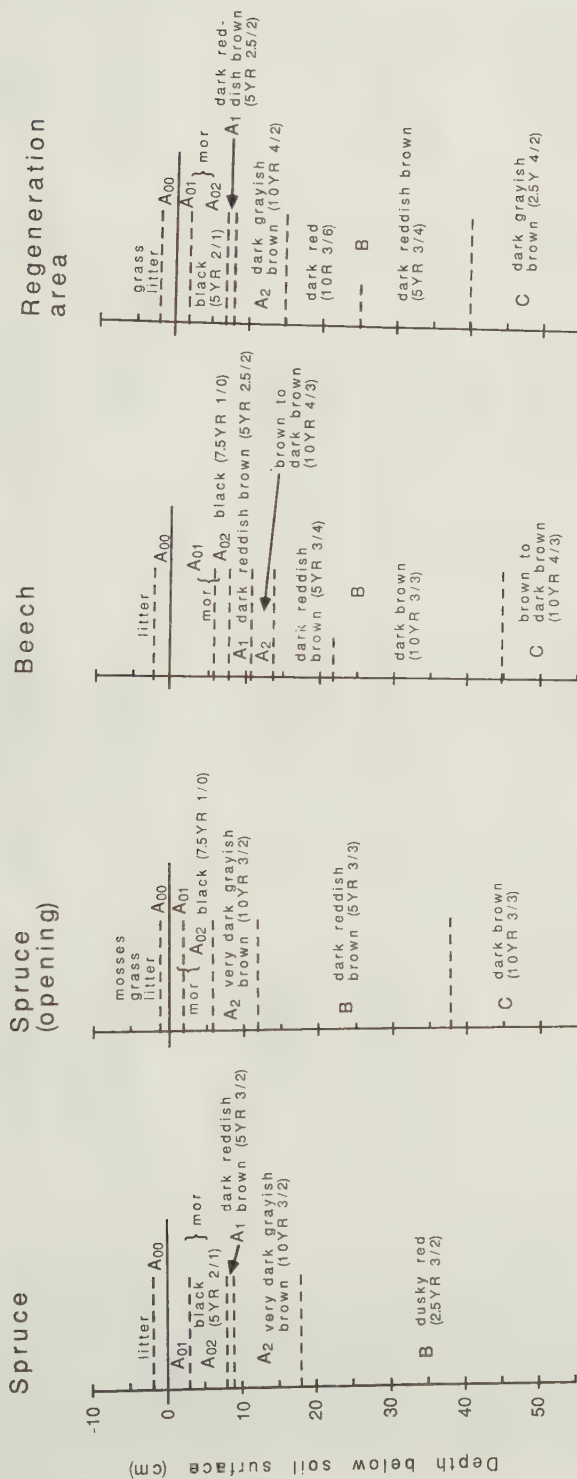


Fig. 1b. Horröd

vertical distribution of organic matter, clay content and pH of the soil profile in Table II and the distribution of metals in Fig. 2.

TABLE II

Content of organic carbon and clay (percent of the dry weight), pH-H₂O and pH-KCl of the studied soils at Horröd and Sjöbo. Sampling period: Sept. 1979

Soil depth,cm	Horröd:				Sjöbo:		
	spruce	spruce (open)	beech	regeneration area	spruce	beech	regeneration area
<i>Organic carbon</i>							
0-5	28	44	19	11	22	3.8	5.5
5-15	6.6	4.9	4.7	3.1	1.9	1.0	1.8
15-35	3.4	2.3	6.4	1.5	1.0	0.6	0.9
35-55	2.3	1.2	2.3	0.5	0.7	1.6	0.3
<i>Clay:</i>							
0-5	2.0	1.4	2.2	2.1	2.1	2.8	3.2
5-15	2.1	3.1	1.7	2.7	3.7	3.0	5.0
15-35	2.1	3.0	1.7	1.8	3.6	3.6	4.3
35-55	2.6	3.9	2.1	1.2	3.5	2.6	3.1
<i>pH-H₂O:</i>							
0-5	3.9	3.9	4.0	4.8	4.0	4.6	4.5
5-15	4.2	4.2	4.3	5.0	4.0	4.7	5.0
15-35	4.4	4.7	4.7	5.1	4.3	4.6	5.0
35-55	4.3	4.5	4.7	4.9	4.5	5.0	4.8
<i>pH-KCl:</i>							
0-5	3.1	2.9	3.1	3.8	3.1	3.6	3.5
5-15	3.5	3.3	3.5	4.0	3.2	3.8	4.2
15-35	3.9	4.1	4.3	4.5	3.8	4.0	4.2
35-55	4.3	4.5	4.4	4.5	4.3	4.2	3.8

The spruce stand at Horröd is even-aged, c. 60 yr (Table I). The vegetation of the forest floor is patchy. An opening (c. 30 x 30 m) in the spruce forest was also studied. A field and bottom layer is usually present. The beech stand is also mainly even-aged, c. 80-100 yr. The trees are unevenly distributed. The vegetation of the forest floor is sparse, growing in patches of the beech leaf-litter. The regeneration area was cleared from trees, (spruce and some Scots pine, *Pinus sylvestris*) in 1970,

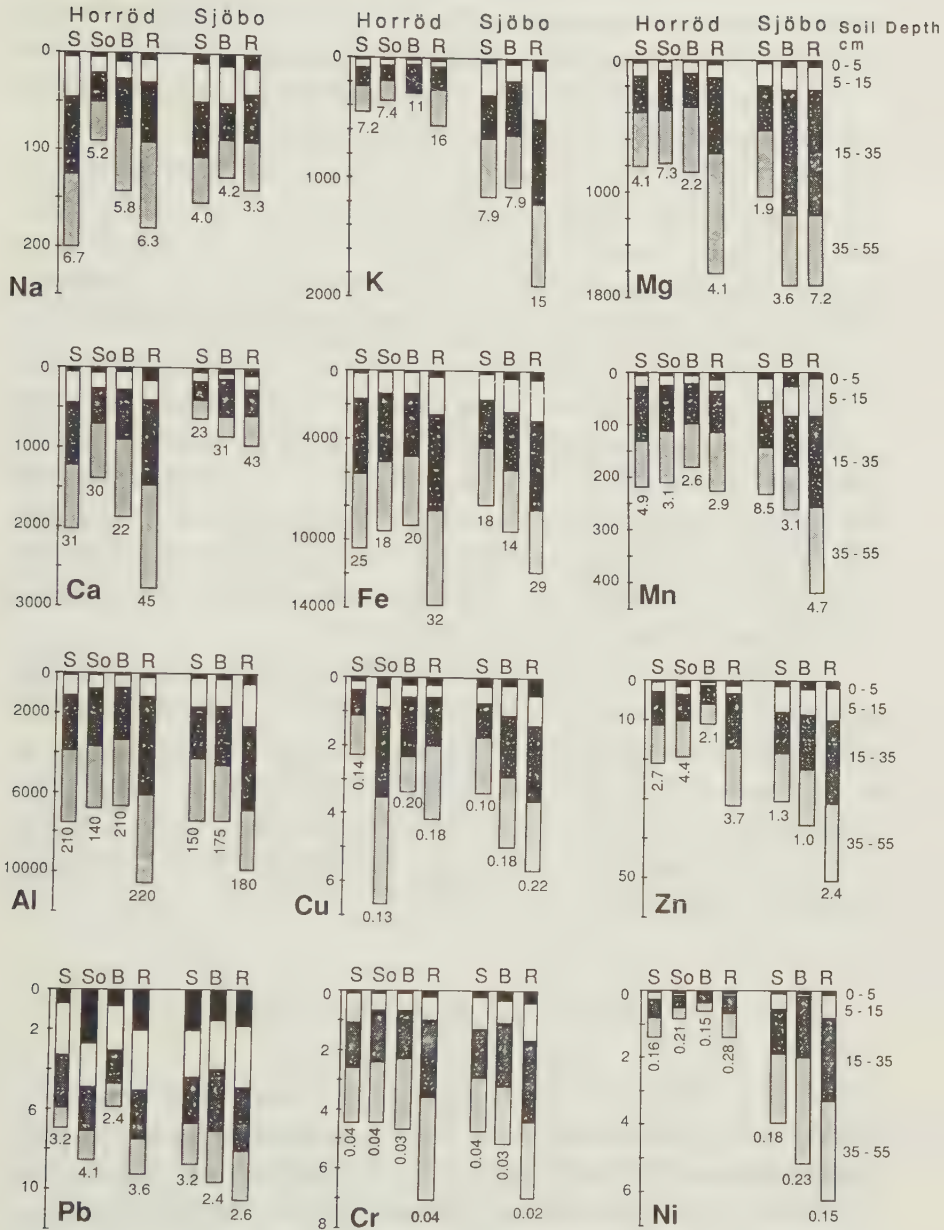


Fig. 2. Content of metals in the studied soils, g m^{-2} . Columns indicate acid digestible amounts ($\text{HNO}_3 : \text{HClO}_4$, 4 : 1) in different soil horizons, figure below each column indicates extractable amount (0-55 cm; Na-EDTA: Cu, Zn, Cd, Pb, Cr, Ni; NH_4Ac (pH 4.8): Na, K, Mg, Ca, Fe, Mn, Al). S=spruce, So=spruce opening, B=beech, R=regeneration area. (Only extractable amount is available for Cd: Horröd, S=0.023, So=0.016, B=0.065, R=0.027; Sjöbo, S=0.023, B=0.023, R=0.028).

eight years before this study started. The vegetation is dominated by grasses, and the dwarf shrub *Calluna vulgaris* is also common.

As beech is more slow-growing than spruce, a beech stand of 80-100 yr roughly represents the same stage of development as a 50-60 yr old spruce stand in this region. There are certain differences between the two localities studied, at Sjöbo a brown forest soil and at Horröd a podzol. The organic top soil is a mull at Sjöbo and a mor at Horröd, indicating a lower mineralization rate of organic matter at the latter site. The soil content of organic matter also differs (Table II). A considerable downward transport of organic compounds and their subsequent precipitation in the upper B horizon has taken place at Horröd, to a lesser degree at Sjöbo. This indicates podzolization processes to be important at Horröd since the downward transport of organic complexes followed by a subsequent precipitation of these in deeper soil horizons, as they become metal saturated, is considered an important prerequisite for podzolization (see Petersen, 1976). One probable reason for these differences in soil properties is differences in the primary mineralogy of the two sites, reflected in a somewhat larger amount of exchangeable base cations, mainly Ca (Table I) and a higher clay content (Table II) at Sjöbo.

The areas studied were extensively utilized during the 19th century for grazing and probably hay-making. Most of the ground at Horröd was cleared from stones probably already prior to the 19th century, today evidenced by scattered fences of stone and moss-covered stone heaps. At Sjöbo stones are lacking.

No sources of pollutants of any great importance to the deposition of acid or metals occur within 40 km of the areas. The areas fulfill the demands of "background" sites of southwestern Sweden.

3. Climate and Weather Conditions

The influence of the Atlantic gives a rather maritime climate to the southwest part of Sweden. The most frequent winds are from the southwest. The main part of the precipitation sum of the year falls in autumn and winter. Mean annual precipitation of the southern study area (Sjöbo) and the northern study area (Horröd) is c. 690 mm and 750 mm respectively according to data from four meteorological stations within 15 km (Elleson, unpublished, pers. comm). The precipitation sum in 1979 was nearly normal (Table III). In 1980-1981 the precipitation sums were c. 25 percent above normal, though differences between seasons were great. Yearly mean summer and winter temperatures during 1979-1981 were usually 1-2 °C below normal. The snow cover is not often stable throughout the winter. However, the four winters from 1978/1979 to 1981/1982 were characterized by a considerable

snow cover (20-50 cm) of above-normal duration. In a normal year, the run-off from the forest stands amounts to c. 300 mm, the mean annual evapotranspiration being c. 60 percent of the precipitation sum.

TABLE III

Precipitation (mm) in the two studied areas, Horröd and Sjöbo, 1979-1981. Mean of four adjacent meteorological stations at each site (in brackets calculated as percent of normal values 1965-1974) (Ellesson, 1985 pers. comm.).

Period	1979	1980	1981	Normal value 1965/74
<i>HORRÖD:</i>				
Jan-March	180 (126)	98 (68)	239 (168)	143
April-June	140 (84)	157 (94)	132 (79)	167
July-Sept	163 (77)	243 (115)	165 (78)	211
Oct-Dec	222 (97)	413 (181)	367 (161)	228
Jan-Dec	705 (94)	911 (122)	903 (121)	749
<i>SJÖBO:</i>				
Jan-March	176 (133)	94 (71)	222 (167)	133
April-June	114 (72)	163 (103)	129 (81)	158
July-Sept	173 (96)	245 (137)	215 (120)	179
Oct-Dec	238 (108)	353 (160)	310 (140)	221
Jan-Dec	701 (101)	855 (124)	876 (127)	691

4. Materials and Methods

Lysimeters were constructed in plexiglass. The diameter of the lysimeters was 290 mm (0-5 and 0-15 cm length) or 190 mm (0-35 and 0-55 cm). One set of lysimeters was installed in each stand. Soil cores from places with freely drained soil were taken vertically from the surface. The cores were taken with steel cylinders and transferred to the lysimeters with a minimum of disturbance. After two supporting plastic cylinders had been installed, the whole units were replaced in their original positions and equipped with Erlenmeyer flasks (Duran glass) for the collection of soil water. Design and installation procedures were originally developed by Tyler (1981) who studied the leaching of several metals from the A horizon below a spruce stand in southernmost Sweden.

Three or four different soil depths were chosen for each set of lysimeters. They represented approximately the $A_{00} + A_0$ horizons, including some moss vegetation (depth 0-5 cm), the A horizon including most of A_2 (depth 0-15 cm), the A horizon + the B_1 horizon (depth 0-35 cm) and, finally, the A horizon + most of the B horizon including B_2 (depth 0-55 cm); see Table I. Installation of the deepest lysimeter (0-55 cm) was made only in those stands where the fluctuations of the ground-water table were expected not to influence this depth. Soil profile terminology is according to Kubiena (1953).

The lysimeters were installed in September 1978 (0-5, 0-15 and 0-35 cm) and in September 1979 (0-55 cm). Sampling started in October 1978 and 1979, respectively, and ceased in December 1981.

Percolates obtained and used for measurements and calculations were never turbid. To minimize the risk of the metal concentrations of the percolates being altered by the installation procedure, the first few samples were omitted. The collection interval was about 1 month, shorter during periods of heavy rain and longer during periods when the soil was frozen or too dry.

Total concentrations of 13 metals in the drainage waters from the lysimeters were measured by AAS technique: Na, K, Mg, Ca, Fe, Mn, Al, Cu, Zn, Pb, Cd, Cr and Ni. Furthermore, pH and dissolved organic carbon (DOC) were determined, DOC by infrared technique using a Beckman 915B carbon analyser. Soil parameters (organic matter, clay content, pH and content of total and extractable amounts of metals) are from soil samples taken from the soil profiles simultaneously with the lysimeter installation. Detailed descriptions of lysimeter installation, field sampling, sample pretreatment and analysis are found in Bergkvist (1986).

5. Results

5.1. DATA PRESENTATION

Data are presented in the following ways: 1) Yearly means of the concentrations of metals, hydrogen ions and dissolved organic carbon, and pH, of soil solutions from various depths; 2) Extractable and "total" amounts of metals in the soils; 3) Metal fluxes and soil budgets.

Concentrations in solutions are calculated as mg l^{-1} for DOC, Na, K, Ca, Mg, Fe, Mn, Al; as $\mu\text{g l}^{-1}$ for Cu, Zn, Pb, Cd, Cr, Ni and H^+ . Metals in soils are calculated as g m^{-2} ; the flux of metals as $\text{g m}^{-2} \text{yr}^{-1}$ and $\text{mg m}^{-2} \text{yr}^{-1}$ for the major and the minor elements, respectively.

5.2. GENERAL CONSIDERATIONS OF THE ELEMENT FLUX CALCULATIONS

Amounts of water collected from the lysimeter soils are over-estimations of the actual situation, due to the use of lysimeter technique (root uptake by the trees is excluded). Therefore, water flows were estimated using a numerical model (Jansson and Halldin, 1980) based on plant and soil properties. For details of the use of the model and for more references, see Bergkvist (1986). Driving variables of the model, air temperature, vapour pressure, wind speed and cloudiness, were taken from national meteorological statistics (SMHI). In addition the most important driving variable, precipitation, was selected from a denser network of meteorological stations (Elleson, pers. comm.). The flux of water used in the calculations of the soil flux of metals was the simulated amounts of run-off water ("percolation") from the model: Horröd a) forest=290 mm yr⁻¹; b) regeneration area=650 mm yr⁻¹; Sjöbo a) forest=300 mm yr⁻¹; b) regeneration area=645 mm yr⁻¹).

5.3. RELEASE AND LEACHING PROCESSES OF SPRUCE, BEECH AND REGENERATION AREAS

The acidity of the soil solution, as pH or H⁺, was the individual parameter best elucidating the ecological influence on soil properties. At comparable soil horizons, soil solutions from the two forest areas studied were consistently most acid in the spruce stands (Figs. 3-5). Soil solutions from the regeneration areas had the highest pH values. After passage of the organic layer and the mineral-A horizon (15 cm soil depth), soil solutions from the spruce stands were the most acid, as an average. The mean pH 3.80 and 3.90 was measured at Horröd and Sjöbo respectively, compared to 4.26 and 4.08 resp. in the beech stands and 4.46 and 4.49 resp. in the regeneration areas. pH of the soil solutions increased continuously down the soil profile. However, the downward pH increase was quite small in the spruce stands. Mean pH of soil solutions from the upper half of the B horizon (35 cm soil depth) in the spruce stands was 4.00 and 4.14 at Horröd and Sjöbo respectively. In the beech stands comparable pH values were 4.27 and 4.31 resp., and in the regeneration areas 4.55 and 4.87 resp. Comparison even deeper in the soil is available from the spruce and beech stands at Sjöbo and from the spruce stand at Horröd (Fig. 5-6). In the lower part of the B horizon soil solution pH from the spruce forest at Horröd increased from c. 4.00 (at 35 cm) to c. 4.20 at 55 cm. At comparable soil depth in the spruce and beech stands of Sjöbo no increase of pH was detected.

The release of dissolved organic matter is considerable in the A horizon of the spruce stands, particularly at Horröd, where the organic mor-layer is thicker than the mull layer at Sjöbo. At 15 cm soil depth the content of DOC of the soil solution was at its peak, c. 150 mg l⁻¹ as yearly mean, while the peak at Sjöbo was found at 5 cm

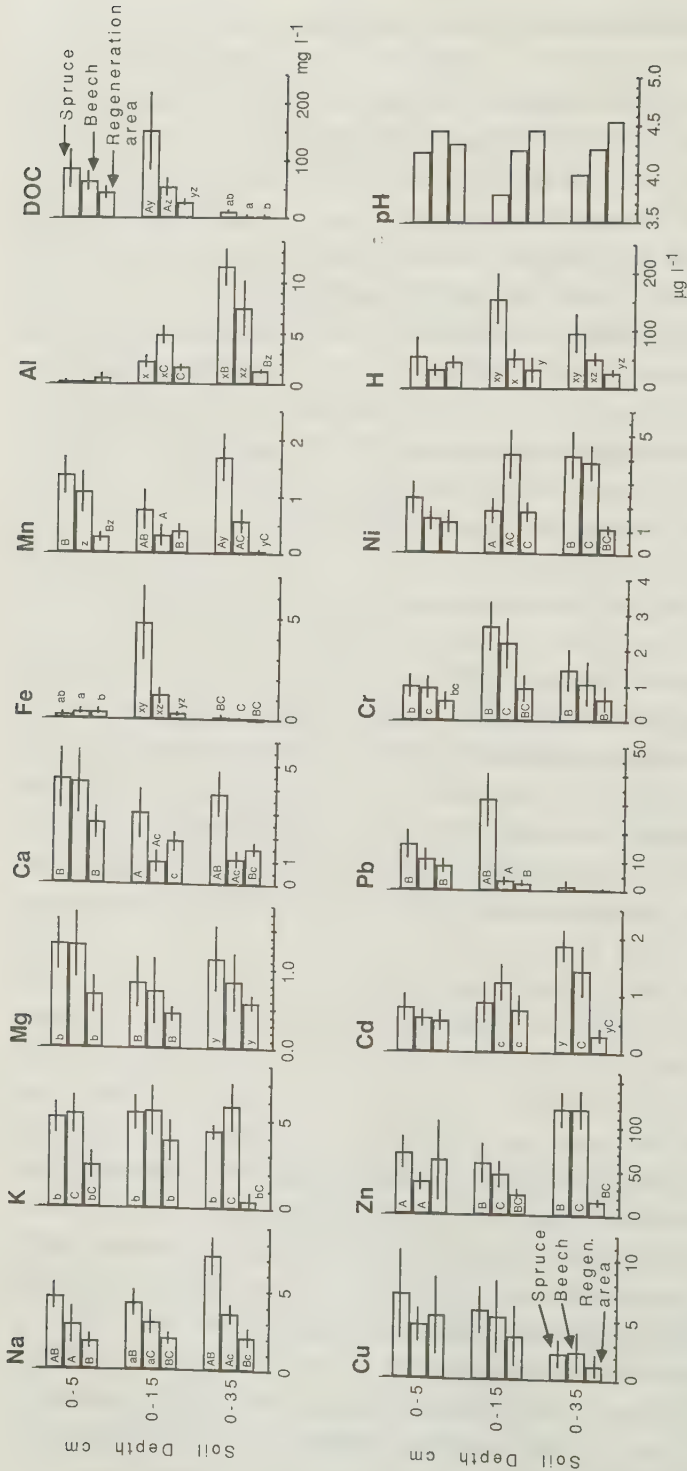


Fig. 3. pH, concentration of metals, DOC and H⁺ in solutions from different depths in the soils of the spruce, beech and regeneration area at Höröd. Means and 95 percent confidence limits of three yr (1979 - 1981); n = 31. Test of the differences between the different stands was made for comparable soil depths, A,a,x denote significant (p < 0.05) differences between the spruce and the beech; B,b,y between the spruce and the regeneration area; C,c,z between the beech and the regeneration area. a,b,c: linear t-test; A,B,C: logarithmic (base e); x,y,z: non parametric (Mann-Whitney) (cf. Sokal and Rohlf, 1981).

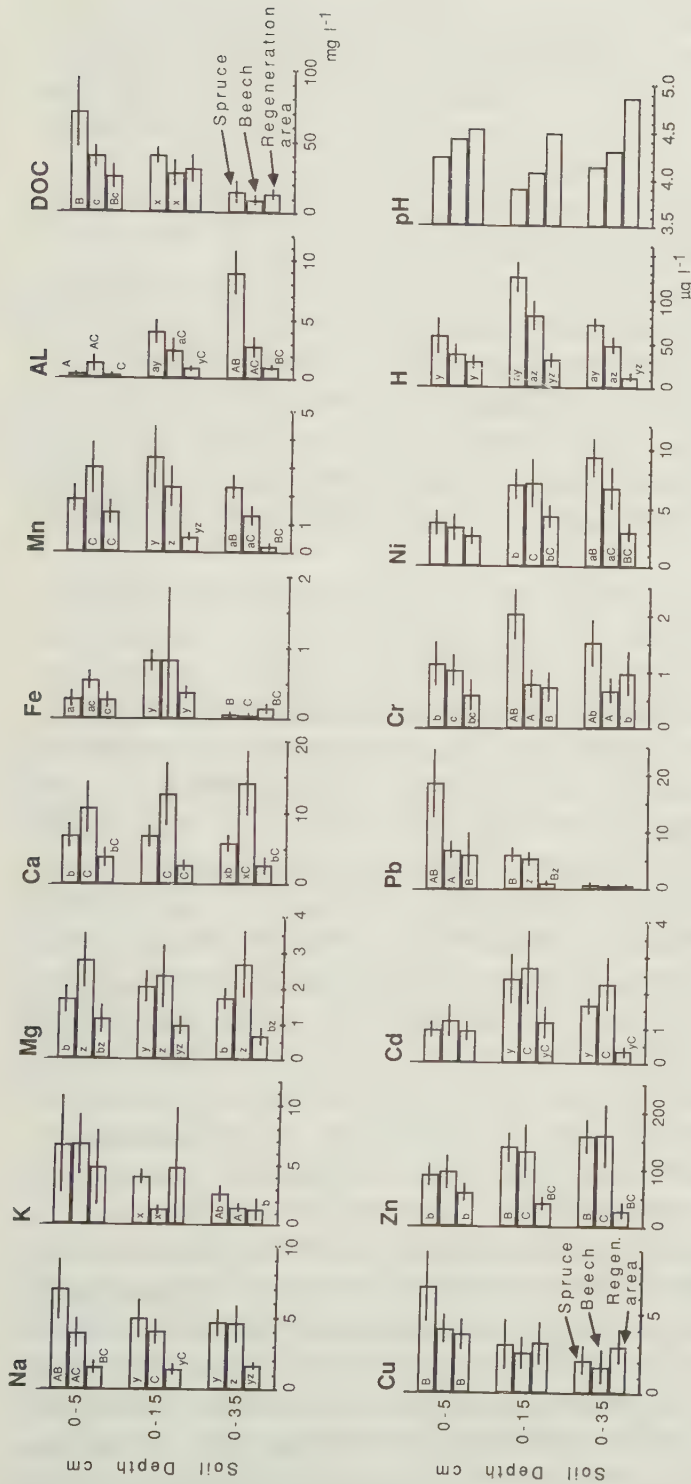


Fig. 4. pH, concentration of metals, DOC and H⁺ in solutions from different depths in the soils of the spruce, beech and regeneration area at Sjöbo. Means and 95 percent confidence limits of three yr (1979 - 1981); n = 31. Explanation of the t-test in Fig. 3.

(c. 75 mg l⁻¹; at Horröd c. 100 mg l⁻¹ at this soil depth). The DOC content of soil solutions from the A horizon of the beech stands and regeneration areas was roughly half that of the spruce stands. In all stands most of the dissolved organic matter precipitated in the upper part of the B horizon (Figs. 3-6). In the lower part of the B horizon very little organic matter was left in the soil solution. It had changed to uncoloured from being dark brown in the A horizon of the spruce stands and light yellowish-brown in the beech stands and in the regeneration areas.

Metal concentrations in soil solutions and the leaching rate from the brown forest soil at Sjöbo were generally higher than in the podzol at Horröd (Fig. 3-4; Table V). Base cations (Na, K, Mg, Ca) were found at higher concentrations and were leached in greater quantities from the brown forest soil, while more Al was leached from the podzol. Also soil solution concentrations of Mn, Zn, Cd and Ni were higher in the brown forest soil, while metals with a leaching related to the leaching of humus (Cu, Pb and Cr) were leached in larger amounts from the podzol, as was DOC.

As a general rule, the lowest soil solution content of metals was found in the regeneration areas of both sites (Figs. 3-4). This is the most conspicuous metal concentration pattern of the soil solutions. The pattern of spruce and beech stands differs somewhat between the two sites. In the podzol at Horröd higher soil solution content of metals was measured in the spruce stand compared to the beech stand (Fig. 3). At different soil horizons this is statistically significant for Na, Ca, Fe, Mn, Al (in deeper horizons), Pb and Ni, with a trend for Mg, Zn and Cr. Only Al and Ni (in the A horizon, 15 cm) show statistically significant higher concentrations in the beech stand. For metals with increasing solution concentrations in deeper horizons, the increase was often more pronounced in the spruce stand (eg. Na, Mg, Ca, Mn, Al, Cd and Ni). In the regeneration area the concentrations of these metals were either unaltered or decreased with increasing soil depth. Soil solutions from the B horizon contained as a mean 11.5, 7.5 and 1.4 mg l⁻¹ of Al in the spruce stand, beech stand and regeneration area, respectively. Comparable concentrations were for Cd 1.9, 1.4, and 0.3 µg l⁻¹. Brooks in the area had the same Cd concentrations as the soil solutions of the regeneration area, but concentrations of the main flow (a small river) were considerably lower.

At Sjöbo, the picture is somewhat different from Horröd. The spruce forest is younger and metal leachability of the brown forest soil higher. The major ions, Ca and Mg, were found to have higher concentrations in solutions from the beech than from the spruce soil. This was also the case for Cd and, in the organic topsoil, Mn, Fe and Al, the latter two metals being statistically significantly higher. In the mineral soil only Ca (at 35 cm) was significantly higher in the beech (Fig. 4). At the deeper (B) horizon (55cm) no metal was found to have higher concentrations in the beech

than in the spruce soil (Fig. 5). Instead, several metals were found in significantly higher concentrations in solutions from the spruce forest (B) horizon, e.g. Mn, Al, Cr and Ni. As was the case at Horröd, the general metal concentration level was lowest in the regeneration area.

In all soils almost all Fe and Pb disappeared together with the organic matter from the soil solution in the B horizon, and so did part of the Cu. In a spruce forest on the Swedish west coast organic species of Al were also shown to precipitate in the upper part of the B horizon together with the organic matter (Nilsson and Bergkvist, 1983). Aluminium in soil solution from the lower B horizon originated mainly from the mineral soil and c. 80 percent of this was an inorganic species. Also in the soils of this study, organic Al species seemed to dominate in the A horizon, according to the high positive correlation between Al and DOC (Table IV). In the B horizon inorganic Al species seemed to dominate, as the correlation between Al and DOC was very weak or negative.

TABLE IV

Correlation coefficients for Al (mg l^{-1}) on DOC (mg l^{-1}) in soil solutions.

Soil depth, cm	spruce	Horröd: spruce (open)	beech	regene- ration area	spruce	Sjöbo: beech	regene- ration area
<i>r</i> (Al on DOC)							
0-5 (n=31) *	0.87***	0.53**	0.83***	0.32	0.80***	0.25	0.64**
0-15 (n=31)	0.82***	0.34	0.20	0.14	0.07	0.94***	0.32
0-35 (n=31)	0.04	0.20	0.00	-0.11	0.01	0.02	0.09
0-55 (n=22)	-0.11	-0.47**	-	-	-0.34	0.14	-

* $p < 0.05$; ** $p < 0.01$; *** $p < 0.001$

The solubility of several metals and the acidity of the soil solution are closely related, as demonstrated by this and other empirical material (Tyler et al., 1985). The relationship between the pH and the total concentration of Al, Mg and Cd, as illustrated in Fig. 7 for the B horizon at Sjöbo, is very close, though non-linear. Similar trends were also obtained for other metals, eg. Ca, Mn, Zn and Ni. There is usually a more or less distinct bend in the curves, indicating a rapidly increasing metal solubility below a particular solution pH. The different stands are placed along the curve. The regeneration areas have the lowest acidity and concentration of

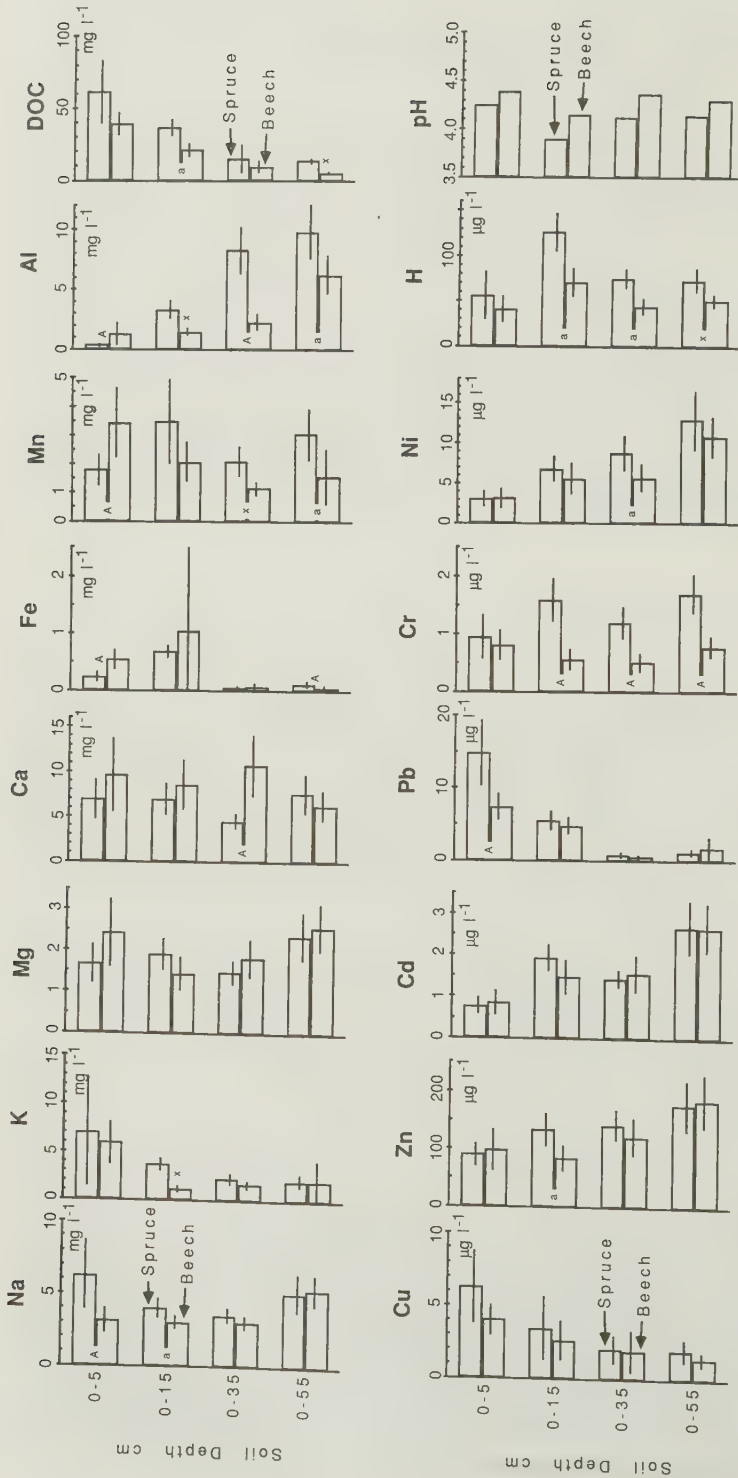


Fig. 5. pH, concentration of metals, DOC and H⁺ in solutions from different depths in the soils of the spruce and beech stand at Sjöbo. Means and 95 percent confidence limits of two yr (1980 - 1981); n = 22. Test of the differences between the different stands was made for comparable soil depths, A, a, x denote significant (p < 0.05) differences between the spruce and the beech. a: linear t-test; A: logarithmic (base e); x: non parametric (Mann-Whitney) (cf. Sokal and Rohlf, 1981).

TABLE V
Fluxes of metals (annual means) in wet deposition and soils of the Horröd and Sjöbo sites (1980-1981).

Soil depth cm	Na	K	Mg	Ca	Al	Fe	Mn	Cu	Zn	Cd	Pb	Cr	Ni
	g m ⁻² yr ⁻¹				mg m ⁻² yr ⁻¹								
HORRÖD:													
Wet dep.*	1.14	0.13	0.15	0.24	0.04	0.05	0.004	0.83	10.5	0.12	8.15	0.18	0.43
Soil solution													
Spruce													
15	1.14	1.10	0.18	1.02	0.35	0.62	0.16	1.08	10.1	0.12	6.00	0.79	0.29
35	1.66	1.20	0.14	0.54	3.18	0.11	0.24	0.45	20.8	0.31	0.39	0.59	0.75
55	1.17	0.61	0.45	0.76	3.14	0.02	0.19	0.33	41.4	0.41	0.56	0.20	1.47
Spruce (open)													
15	0.55	0.19	0.24	1.18	0.22	0.21	0.19	0.89	22.6	0.31	1.31	0.10	0.38
35	0.39	0.30	0.22	0.62	0.91	0.01	0.12	0.27	18.9	0.28	0.17	0.56	0.52
55	0.64	0.22	0.22	0.89	0.63	0.01	0.13	0.38	23.4	0.23	0.32	0.12	0.66
Beech													
15	1.07	1.40	0.23	0.27	1.29	0.32	0.10	0.89	12.1	0.35	1.05	0.72	1.07
35	0.65	1.61	0.24	0.18	2.30	0.03	0.14	0.41	31.9	0.38	0.15	0.62	0.76
Regen. area													
15	1.14	1.74	0.28	1.02	1.02	0.17	0.21	1.53	13.2	0.27	1.44	0.36	0.93
35	1.07	0.24	0.32	0.86	0.92	0.01	0.04	0.74	8.5	0.13	0.30	0.25	0.64
SJÖBO													
Wet dep.*	1.09	0.12	0.15	0.22	0.04	0.05	0.004	0.80	10.0	0.11	7.79	0.17	0.41
Soil solution													
Spruce													
15	1.10	0.92	0.56	1.63	0.92	0.20	0.87	0.66	34.4	0.47	1.71	0.43	1.54
35	0.96	0.55	0.45	1.10	2.40	0.02	0.58	0.52	38.0	0.37	0.21	0.32	2.02
55	1.38	0.53	0.69	2.16	2.79	0.03	0.84	0.54	48.5	0.70	0.35	0.48	3.19
Beech													
15	0.91	0.30	0.37	1.93	0.38	0.12	0.49	0.95	19.6	0.34	1.22	0.12	1.17
35	0.86	0.39	0.49	2.36	0.56	0.02	0.32	0.40	30.1	0.35	0.17	0.13	1.20
55	1.45	0.32	0.72	1.69	1.79	0.01	0.36	0.37	46.1	0.69	0.30	0.23	2.61
Regen. area													
15	0.80	0.92	0.55	1.56	0.66	0.25	0.32	1.56	21.9	0.50	0.64	0.43	2.45
35	0.99	0.44	0.30	1.17	0.66	0.11	0.12	1.51	19.5	0.16	0.31	0.46	1.46

* Calculated from average concentrations of the region (Bergkvist, 1986)

metals, followed by the beech and the spruce stands, the two latter often intermingled. In all soils studied in both areas the critical acidity of the soil solution in the B horizon is within the pH range of 4.0 - 4.5, as a drastic change of the metal solubility in the mineral soil occurs within this range. An increased soil acidity in the brown forest soil at Sjöbo was mostly buffered by Al release in the spruce stand, while the release of base cations (only Mg is shown in Fig. 7) was acting as the main buffer in the soils of the beech and the regeneration area. In the spruce stand a drop in soil solution pH by 0.2 units in this range results in a 5- to 10-fold increase of the Al concentration. In the beech stand and in the regeneration area, Mg and Cd were increased by 3 to 5 times at a corresponding pH drop. In the soil solution of the regeneration areas the pH is mostly above this range, while it is frequently within the range in the beech and without exceptions within the range in the spruce stands. This is also reflected in a higher general level of particularly the Al concentration in the spruce stands.

5. 4. EFFECT OF SPRUCE CANOPY COVER ON SOIL SOLUTION CHEMISTRY

The spatial variability in soil solution composition and the leaching of metals within a stand is considerable. One very important controlling factor is the degree of canopy cover, which affects e.g. the composition of precipitation water reaching the soil. It is also of great importance to the litterfall and light flow, which in turn affect the vegetation of the forest floor. In the spruce forest at Horröd an opening (c. 30x30 m) was studied in addition to the canopy-covered plot (Fig. 6). Throughfall water reaching the canopy-covered soil was considerably more acid than the precipitation reaching the soil in the opening, pH 3.70 and 4.20 respectively. Sulphur and nitrate deposition (not measured in this study) is also several times greater beneath a spruce canopy than outside (Bergkvist et al., 1986), as is the deposition of most elements.

Metal concentrations of soil solutions percolating the canopy-covered lysimeters were with very few exceptions significantly higher than in the opening. In fact the only metal that had a statistically significantly higher concentration in solutions from the opening than from the canopy-covered soil was Cd in the very acid mineral A horizon (15 cm). All other metals were either equally or more concentrated in soil solutions from the canopy-covered plot. Higher solution concentrations had particularly Al, but also Na, K, Fe, Mn, Zn, Pb and Ni in various horizons.

The input of litter and the thickness of the organic top-layer is smaller in the opening. The transport of dissolved organic matter was also significantly lower than in the canopy-covered plot. This was probably the reason for the lower transport of Fe and Al in the A horizon of the opening, as these metals are mainly transported as

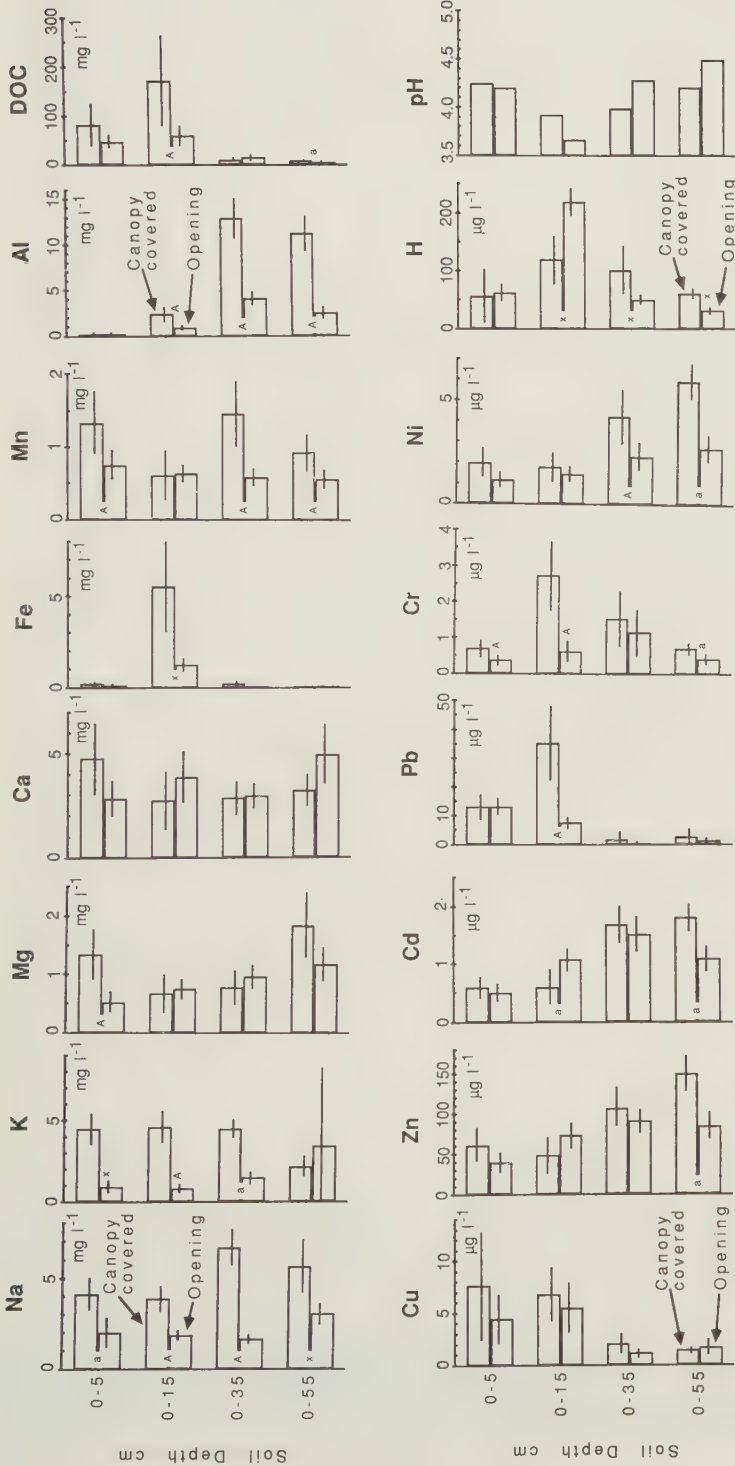


Fig. 6. pH, concentration of metals, DOC and H^+ in solutions from different depths in the soil of the spruce forest at Horröd; a canopy covered plot and a plot in an opening outside the canopy. Means and 95 percent confidence limits of two yr (1980 - 1981); $n = 22$. Test of the differences between the different plots was made for comparable soil depths, A, a, x denote significant ($p < 0.05$) differences. a: linear t-test; A: logarithmic (base e); x: non parametric (Mann-Whitney) (cf. Sokal and Rohlf, 1981).

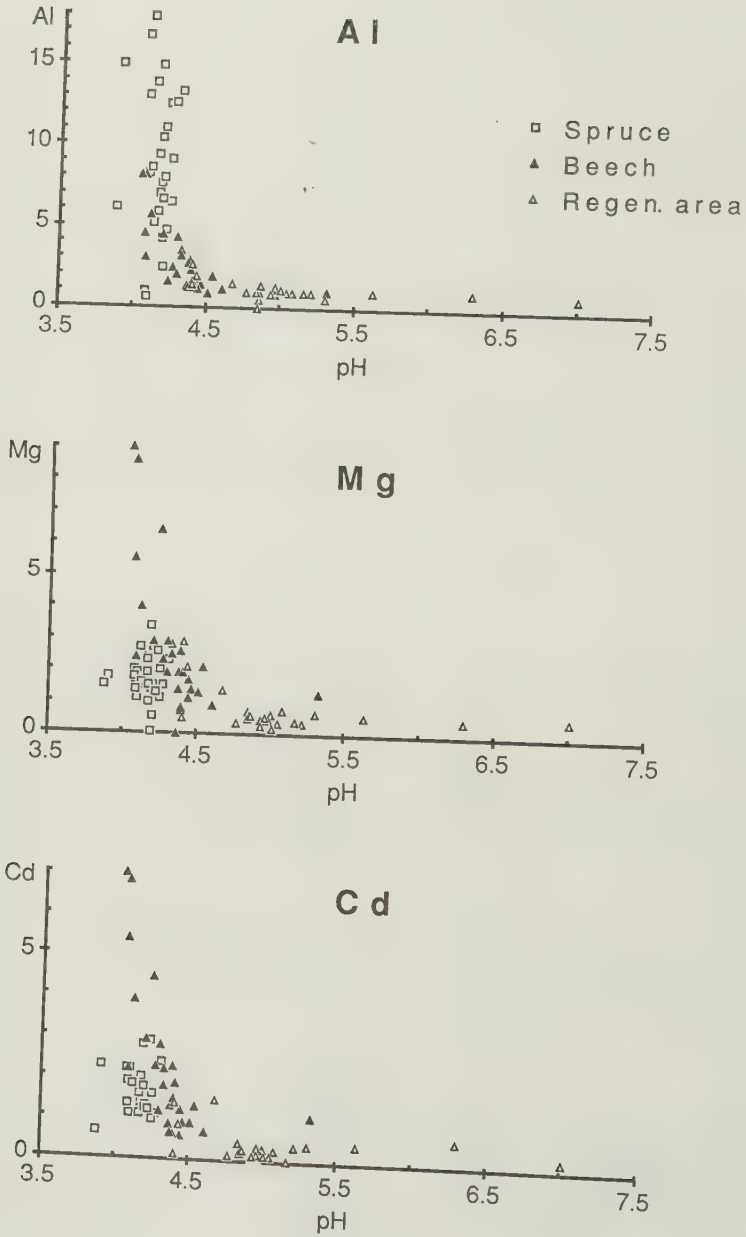


Fig. 7. The relationship between pH and the concentration of Al, Mg (mg l^{-1}) and Cd ($\mu\text{g l}^{-1}$), respectively, in soil solutions from the upper B horizon (35 cm) in the spruce, beech and regeneration area at Sjöbo.

organic complexes in this horizon. This was probably also the reason for the lower soil transport of Pb, Cu and to a certain degree Cr in the opening. Also from the B horizon (at 55 cm) the leaching of several metals was highest in the canopy-covered plot, eg. of Al, Mg, Zn, Ni and Cd (Table V).

5.5. SOIL BUDGETS

Mineral soil fluxes of metals were calculated using the simulated flow of run-off water (Table V), and compared to the store of metals, as shown in Table VI, for the upper B horizon (B₁ 15-35 cm soil depth) and Table VII for the entire B horizon (15-55 cm depth). The mineral soil budget is considered positive if the input at 15 cm is greater than the outflow at 35 cm depth. Due to lack of dry deposition data for all vegetation types, no ecosystem budgets were calculated. Dry deposition rates to spruce forests were estimated by the experiment and model approach by Wiman (1984), and from these estimations the dry deposition to a mature spruce forest was calculated in a previous paper (Bergkvist, 1986). Due to the smaller aerosol trapping area (particularly when the trees are defoliated in winter), the dry deposition to a beech stand ought to be considerably lower than to a spruce stand (Höfken and Gravenhorst, 1982; Mayer and Ulrich, 1982). Also to the regeneration area the dry depositon is likely to be much smaller than to a spruce stand. The great importance of dry deposition to the total input of certain elements to forest ecosystems makes calculations of ecosystem budgets using only the wet part of the total deposition basically unreliable. However, at the current state of knowledge it is not possible to accurately quantify the dry deposition to the different vegetation types in this study, as direct measurements are lacking (Lindberg and Harris, 1981; Lindberg and Lovett, 1985; Lindberg et al., 1986). It was also shown that at least in some areas (though probably not in those of the present study) cloud droplet deposition of certain elements to forest ecosystems could be more important than bulk deposition (Lovett et al., 1982).

5.5.1. *Horröd*

The flow pattern of metals (Table V; VI; VII) in the soils differs somewhat from the concentration pattern given above (Figs. 3-6). Due to the greater flux of soil water in the regeneration area, the calculated metal flux through the soil will not be as low, compared to the forest stands, as would be expected from concentrations. However, in the regeneration area all metals showed a net accumulation or were at equilibrium in the mineral soil (15-35 cm; Table VI). In the forest stands K, Al, Mn, Zn and Cd were lost from the mineral soil, as were also Na and Ni in the spruce stand. In all

TABLE VI

Annual metal budgets of the mineral soil (15 to 35 cm depth) in the two forest areas (in brackets the exchangeable* and the "total"*** soil pool of metals). "+" denotes an increase (gain) and "-" a decrease (loss).

HORRÖD

Spruce

Beech

Regeneration area

(g m⁻² yr⁻¹)

Na	-0.52	(2.2; 79)	0.42	(2.2; 50)	0.06	(2.2; 61)
K	-0.11	(2.2; 150)	-0.21	(2.5; 88)	1.5	(4.8; 182)
Mg	0.05	(0.5; 265)	±0.0	(0.2; 257)	-0.04	(0.4; 568)
Ca	0.48	(4.4; 770)	0.09	(4.3; 602)	0.16	(6.1; 1060)
Al	-2.83	(79; 2730)	-1.01	(93; 2550)	0.1	(111; 4890)
Fe	0.51	(16; 4400)	0.28	(3.4; 3610)	0.16	(4.4; 5570)
Mn	-0.08	(0.6; 103)	-0.03	(0.3; 76)	0.17	(0.4; 78)

(mg m⁻² yr⁻¹)

Cu	0.63	(50; 700)	0.49	(60; 1700)	0.79	(30; 1400)
Zn	-11	(800; 8100)	-20	(600; 4200)	4.72	(1500; 13700)
Cd	-0.2	(9; -)	-0.03	(13; -)	0.15	(8; -)
Pb	5.6	(900; 2600)	0.9	(300; 1600)	1.14	(300; 2400)
Cr	0.2	(17; 1500)	0.11	(17; 1600)	0.11	(22; 2600)
Ni	-0.46	(50; 520)	0.31	(50; 250)	0.29	(100; 500)

SJÖBO

Spruce

Beech

Regeneration area

(g m⁻² yr⁻¹)

Na	0.14	(1.4; 56)	0.05	(1.6; 37)	-0.2	(1.4; 48)
K	0.37	(1.9; 352)	-0.1	(3.6; 445)	0.48	(4; 706)
Mg	0.12	(0.2; 335)	-0.12	(0.3; 945)	0.24	(1.2; 638)
Ca	0.53	(4.0; 219)	-0.43	(10; 453)	0.39	(14; 328)
Al	-1.48	(66; 2570)	-0.18	(80; 2970)	±0.0	(81; 4210)
Fe	0.18	(7.8; 2830)	0.1	(5; 3360)	0.15	(7.1; 5140)
Mn	0.29	(0.7; 89)	0.17	(0.4; 94)	0.2	(1.1; 175)

(mg m⁻² yr⁻¹)

Cu	0.13	(40; 960)	0.55	(40; 1800)	0.05	(80; 2200)
Zn	-3.56	(300; 10100)	-10	(300; 13700)	2.4	(700; 21000)
Cd	0.09	(7; -)	-0.02	(8; -)	0.34	(8; -)
Pb	1.5	(600; 2300)	1.05	(600; 3100)	0.33	(500; 3200)
Cr	0.11	(13; 1600)	±0.0	(18; 2100)	-0.03	(18; 2700)
Ni	-0.47	(70; 1300)	-0.03	(80; 1800)	0.98	(40; 2440)

* Na-EDTA extractable: Cu, Zn, Cd, Pb, Cr, Ni; NH₄Ac (pH4.8)-extractable: Na, K, Mg, Ca, Al, Fe, Mn

** Digestion with conc. HNO₃ : HClO₄ (4:1)

soils the budget of Mg was at equilibrium, while Ca was accumulating. Also Fe, Cu, Pb and Cr together with organic matter were accumulating in the mineral soil of all stands.

More Al, Mn, Cd and Ni was lost from the mineral soil of the spruce than of the beech stand, whereas the reverse was true for Zn. The annual loss of Mg from the entire B horizon (15-55 cm depth) of the spruce stand were c. 10 percent of the currently acid NH_4Ac exchangeable soil pool (Table VII).

5.5.2. *Sjöbo*

Also at Sjöbo, all metals were accumulating or at equilibrium (except Na) in the mineral soil (15-35 cm) of the regeneration area (Table V; VI). Only Al and Zn were lost from the mineral soil of both forest stands; Al considerably more from the spruce soil and Zn more from the beech soil. In the spruce stand the only other metal lost from the mineral soil was Ni, which was at equilibrium in the mineral soil of the beech stand. Net losses from the latter were recorded also for K, Mg and Ca.

Iron, Cu and Pb were accumulating in the soil of all three vegetation types. An important proportion (nearly half) of the acid NH_4Ac extractable amount of Mg was leached each year from the beech forest, indicating the potential risk of Mg deficiency to the trees if the replenishment of the exchangeable store does not keep pace with leaching and uptake.

In the spruce and the beech stands at Sjöbo, lysimeters down to 55 cm soil depth were installed. From the entire (B) horizon (15-55 cm depth) a net loss of all metals studied, except K, Ca (from the beech soil), Fe, Mn, Cu and Pb was recorded in both forest ecosystems. Calcium and Al were lost in significantly larger amounts from the spruce ecosystem, as was Mg from the beech ecosystem, the other metals in approximately equal amounts from the two stands (Table VII).

6. Discussion

The leachability of metals in the soil is strongly influenced not only by the vegetation type but also by the soil type. The properties of the soils differ between the localities studied, a brown forest soil at Sjöbo and a podzol at Horröd. Different buffer systems are acting to neutralize protons deposited to the soil or produced within it. The proportion of cations released indicates which buffer system is acting. In the brown forest soil the buffering action to a large extent resulted in the release of Ca and Mg. Together with the pH value of soil solutions (in the (B) horizon: 4.2 to 5.0) this indicates that the soil is within the cation exchange buffer range recognized by

TABLE VII

Annual metal budgets of the mineral soil (15 to 55 cm depth) in the two forest areas (in brackets the exchangeable* and the "total"*** soil pool of metals). "+" denotes an increase (gain) and "-" a decrease (loss).

HORRÖD

	Spruce		Spruce (opening)	
(g m ⁻² yr ⁻¹)				
Na	-0.03	(3.8; 155)	-0.09	(4.1; 70)
K	0.49	(3.4; 373)	-0.03	(2.1; 296)
Mg	-0.26	(0.7; 686)	0.02	(0.6; 697)
Ca	0.25	(7.1; 1580)	0.29	(6.5; 1124)
Al	-2.79	(199; 6440)	-0.42	(124; 6000)
Fe	0.6	(18; 8880)	0.2	(5.6; 8090)
Mn	-0.03	(0.9; 193)	0.06	(0.3; 185)
(mg m ⁻² yr ⁻¹)				
Cu	0.75	(90; 1900)	0.51	(20; 5800)
Zn	-31	(1400; 18200)	-0.78	(1600; 15900)
Cd	-0.29	(16; -)	0.09	(4; -)
Pb	5.43	(1100; 3700)	0.99	(500; 3700)
Cr	0.59	(30; 3400)	-0.02	(20; 3800)
Ni	-1.19	(110; 1160)	-0.28	(120; 690)

SJÖBO

	Spruce		Beech	
(g m ⁻² yr ⁻¹)				
Na	-0.28	(2.2; 105)	-0.54	(2.7; 77)
K	0.39	(3.1; 853)	-0.03	(4.9; 893)
Mg	-0.13	(0.3; 847)	-0.35	(0.5; 1485)
Ca	-0.53	(6.3; 472)	0.24	(14; 719)
Al	-1.87	(122; 5750)	-1.4	(130; 5830)
Fe	0.17	(12; 6220)	0.11	(7; 7070)
Mn	0.03	(1.1; 181)	0.13	(0.6; 180)
(mg m ⁻² yr ⁻¹)				
Cu	0.12	(70; 2660)	0.58	(110; 3900)
Zn	-14	(500; 22700)	-26	(500; 28200)
Cd	-0.24	(13; -)	-0.36	(16; -)
Pb	1.36	(800; 4400)	0.92	(900; 5700)
Cr	-0.04	(25; 3500)	-0.11	(28; 4100)
Ni	-1.6	(130; 3400)	-1.45	(160; 5000)

* Na-EDTA extractable: Cu, Zn, Cd, Pb, Cr, Ni; NH₄Ac (pH4.8)-extractable: Na, K, Mg, Ca, Al, Fe, Mn

** Digestion with conc. HNO₃ : HClO₄ (4:1)

Ulrich (1983). In the podzol at Horröd significant release of Al occurred and the pH value of soil solution from the B horizon was frequently below 4.2, indicating the soil to be within the aluminium buffer range. The different chemical states of the soils were also indicated by the exchangeable amounts of Ca and Al in the B horizon. In extractions with acid NH_4Ac , Ca dominated at Sjöbo while Al was more important in the Horröd soil. Comparison of soil pH shows that most of the H^+ in the lower B horizon at Horröd was in the solution (almost 100 percent in the acid spruce stand). The same pH as with H_2O , or only slightly lower, was measured after extraction with 0.2 M KCl. Aluminium ions seem to occupy all cation exchange positions almost completely in the podzol. This is evidently not the case at Sjöbo. At comparable soil depth in the brown forest soil, significantly more hydrogen ions were extracted with KCl than with H_2O , at least in the beech and the regeneration areas.

The leachability differs more between the open regeneration area and the two forest types than between the latter. From the regeneration areas with mainly grass vegetation, the loss of metals was considerably lower than from the forests, in spite of some possible over-estimation of the true run-off rates from the grass-swards by the model used. In both sites the soil of the regeneration area mainly released Ca and Mg, indicating these stands to be within the cation exchange buffer range. This is also indicated by the pH of the soil solutions. Spruce seems to exert a more powerful influence than beech on the leachability of metals in soils, but also beech increases the release of some metals considerably. At Horröd the soil in both the spruce and the beech stand is leaching significant amounts of Al, while at Sjöbo it was only in the spruce stand that the buffering reaction resulted in the leaching of Al; also the pH of the soil solutions corresponds to the aluminium buffer range. The A_2 horizon and the uppermost part of the B horizon in the spruce forest at Horröd was characterized by a considerable leaching of Fe. As the amount of dissolved organic matter was large, the solubility of iron at the prevailing pH (3.8 as an average) becomes high enough for Fe to be released in these quantities and transported to the B horizon as Fe-organic complexes. This part of the soil lies on the boundary to the iron buffer range, which leads to podzolization. As the soil acidity increased, cation exchange seemed to be the most important buffer action in the beech forest soil at Sjöbo, as was shown by the considerable leaching of Ca and Mg, and the simultaneous low leaching rate of Al.

Spruce canopies are known to lower the pH of incident precipitation, whereas beech canopies increase it, at least in rural areas (Nihlgård, 1970; Mayer and Ulrich, 1977; Bergkvist et al. 1986). Also the internal annual production of acids differs between vegetation types. In a spruce stand in W. Germany the total annual H^+ -load from deposition and internal sources was about twice the H^+ -load in a beech stand

(Matzner and Ulrich, 1981). The influence of the canopies on element deposition to the forest floor varies greatly with forest structure and soil fertility, and with the pollution load (Nihlgård, 1970; Astrup and Bülow-Olsen, 1979; Heinrichs and Mayer, 1980). There was always a considerable increase in element content when incident precipitation had passed the spruce canopy. In beech stands, several elements were instead caught by the canopy. The ratio between spruce and beech, for throughfall concentration of elements, varies from c. 2:1 to 4:1. To some extent, however, this might be due to evaporative concentration of the rainwater caused by a greater degree of interception by spruce.

However, beech is more slow-growing than spruce, attaining maturity at a higher age. The cumulated input and production of acids of an entire generation might not differ greatly between stands of spruce and beech, but in spruce it is produced in a shorter time interval. As the spruce stands were chronologically younger (but not with respect to stage of development) than the beech stands in this study, the acidifying influence of spruce seems to have a higher potential (see e.g. Nihlgård, 1971). The pedological influence of both the spruce and the beech seems to penetrate deeper into the soil in Horröd than in Sjöbo, this being evidenced not only in the physical and chemical characteristics of the soil but also in element dynamics. If the upper soil horizons are already in the aluminium or iron buffer range, additional soil acidification may result in changes in the chemical state of deeper horizons, this being evidenced by release of base cations, accumulation of Al ions and a pH decrease.

To summarize, higher internal annual production of acid in combination with a higher deposition rate of acidifying substances to a spruce forest compared to a beech forest or an open area, is the probable explanation for the higher soil solution concentration and the greater losses of metals from the mineral soil in the spruce stands studied, compared to the adjacent stands with beech or regeneration areas. Matzner and Ulrich (1981) regard the soil of spruce and beech forests in W. Germany as sinks for H^+ and S and sources for Ca, Mg, Mn and Al. It may be postulated that the increased soil acidification documented by Falkengren-Grerup (1985) and Hallbäck and Tamm (1985) will have significantly increased the leaching rate of various metals in soils of S Sweden with different types of vegetation. Examples are Ca, Mg, Mn, Al, Zn, Cd, and Ni.

Preliminary results from a current study (unpublished) of metal leaching rates from the "C horizon" (110 cm soil depth) of the soils studied may be compared with the outflow recorded from the B horizon (55 cm depth). They indicate that the pedological influence goes very deep in the glacial till at Horröd derived from acid igneous rocks. In the spruce stand the soil solution acidity continued to increase downward in the morphological C horizon, whereas in the beech stand the acidity

was slightly decreased, and in the regeneration area the decrease was considerable between 55 and 110 cm. Concentrations of metals were unaltered or decreased only slightly in the depth interval 55 - 110 cm of the spruce stand, but decreased significantly in the same interval of the beech stand and the regeneration area. Zinc was an exception; a considerable increase of solution concentration was shown in both the spruce and the beech stand down to 110 cm. The soil at Sjöbo, derived from an originally more calcareous glaci-fluvial sand, seemed to buffer the acidity much more efficiently. pH increased significantly downward in the "C horizon" in all plots, the increase being highest in the beech stand. All metals had decreasing soil solution concentrations downward in the "C horizon". Most pronounced was the decrease in the beech stand, as was also the case with the (B) horizon.

Comparisons of spruce and beech forests are available from the more heavily polluted Solling mountains in W. Germany, though the parent material of these soils is mainly different from that of south Sweden (Heinrichs and Mayer, 1977; 1980; Seekamp, 1977). The gross outflow from the rooting zone of Na, K, Mg, Ca, Mn, Fe, Cr and Cd was on the same general level as in this study, whereas Cu, Zn and Pb were leached in larger amounts in Solling. Aluminium and Ni were leached in much larger amounts from the soils of this study. The deposition load was considerably greater in Solling. Therefore, metals with few exceptions showed a net accumulation within the ecosystems.

The large particle deposition load to the forest soils at Solling is combined with a very high acidity in precipitation. Beneath the spruce canopy the annual mean pH was 3.4, compared to 3.8 beneath the beech canopy (Mayer and Ulrich, 1977). In south Sweden comparable pH values are 3.7 and 4.7 respectively. Soil solution concentrations of metals were also generally higher in the spruce than in the beech forest at Solling.

7. Conclusions

Emerging from conditions prevailing in south Sweden, the conclusion is that both the soil type and the vegetation type seem to be of great importance for the soil acidification and the metal leaching rates:

1. The loss of base cations (and the leaching rates of several other metals) is greater from a brown forest soil (lying in the cation exchange buffer range) than from a more acid podzol (lying in the aluminium buffer range). The reverse is true of Al.

2. The soil in the open regeneration areas is much less acid and the leaching rates of metals are much lower than in the the adjacent spruce or beech stands with the same parent mineral soil.

3. The soil acidity is greater and penetrates deeper in spruce stands than in adjacent beech stands with the same parent mineral soil.

4. The brown forest soils of spruce and beech forests are in different chemical states. In a spruce stand, soil acidity is mainly buffered by Al release, while cation release is the main buffer reaction in a beech stand with the same parent mineral soil.

5. The soil solution concentrations of metals are usually, though not always, higher in the spruce stands than in the adjacent beech stands, as are the net losses of many metals.

6. Below a spruce canopy, the deeper soil horizons are distinctly more acid and the leaching rates of metals considerably greater than in an opening in the forest.

It is reasonable to claim that the use of less acidifying tree species than spruce, in areas exposed to air pollutants, would reduce nutrient losses from soils and counteract soil acidification. However, if the acid deposition were reduced the acidifying influence of spruce would also diminish.

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